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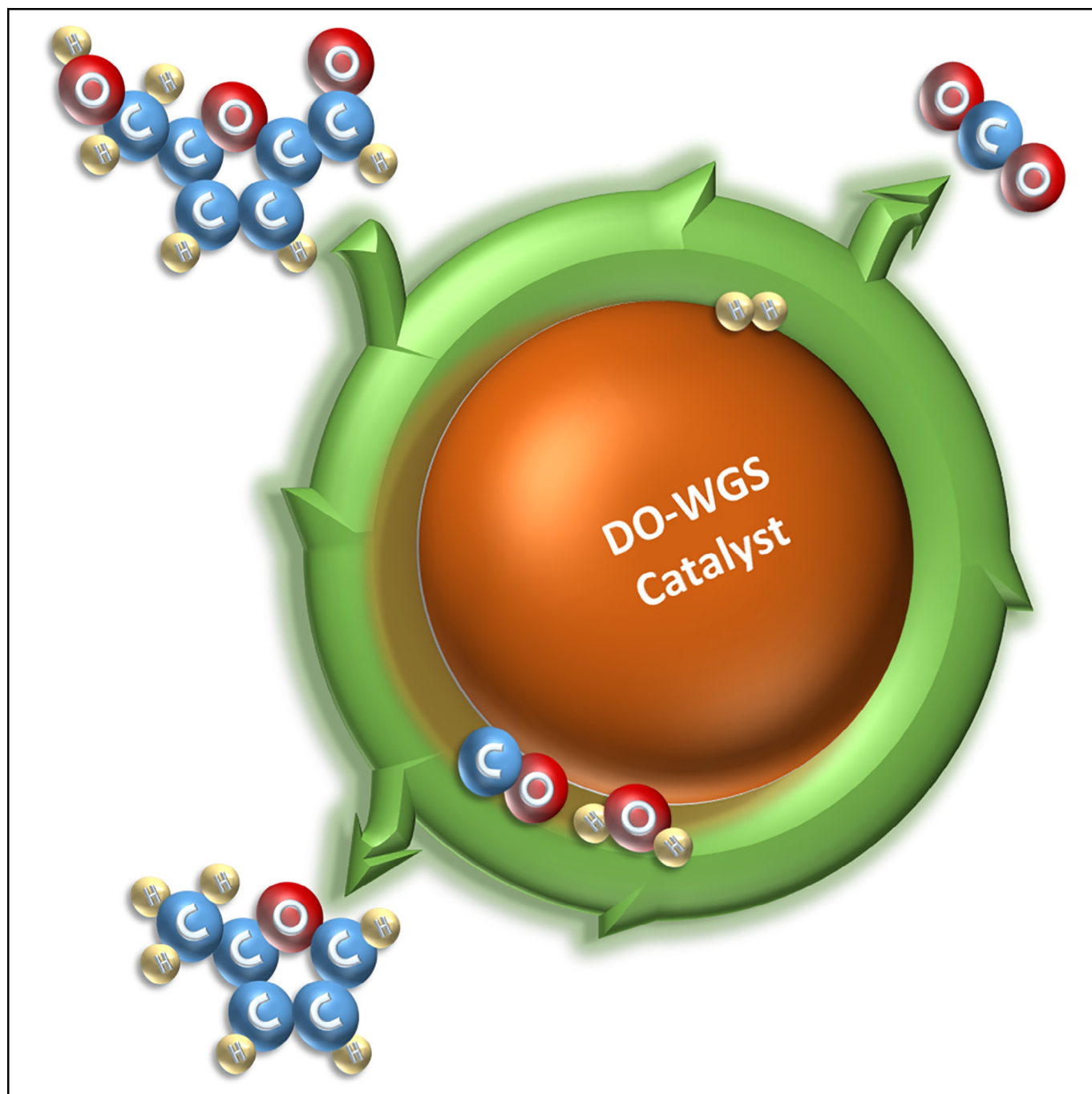
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Selective Deoxygenation of Biomass-Derived Bio-oils within Hydrogen-Modest Environments: A Review and New Insights

Kyle A. Rogers^[a] and Ying Zheng^{*[a, b]}



Research development of processes for refining bio-oils is becoming increasingly popular. One issue that these processes possess is their high requirement for H_2 gas. In response, researchers must develop catalysts that perform deoxygenation while minimizing H_2 consumption—selective deoxygenation. Unlike traditional deoxygenation processes, selective deoxygenation reactions and catalysts represent an information gap that, prior to this publication, has yet to be reviewed. This review addresses the gap by providing both a summary of recent research developments and insight into future developments of new catalytic materials. Bifunctional catalysts contain-

ing a combination of oxophilicity and an active metal phase appear to be the most beneficial for selective deoxygenation processes in a H_2 -modest environment. It is important that catalysts have a supply of disassociated hydrogen, because without such, activity and stability will suffer. The authors recommend to maximize the use of internally available hydrogen in bio-fuel, which may be the only viable approach for deoxygenation if external H_2 gas is limited. This would be possible through the development of catalysts that promote both the water–gas-shift and deoxygenation reactions.

1. Introduction

Within recent years, there has been increasing interest in the development of biofuels. The reason for such has been argued to be due to the threat of global climate change and a shortage of oil reserves.^[1] It is in the best interest of the current society that engineers and scientists endeavor to develop new, sustainable energy resources whilst reducing greenhouse-gas emissions. Within the transportation industry, biofuels are the only carbon-neutral alternatives, and they are becoming increasingly important, as they possess the potential to be incorporated into the existing infrastructure.^[2]

Some biofuels have already begun to merge into the transportation industry, including bioethanol and biodiesel composed of fatty acid methyl esters (FAMES). There are, however, concerns about these first-generation biofuels. First, they cannot totally replace fossil fuels—gasoline and diesel—owing to differences in properties such as reduced energy densities and viscosities at low temperatures.^[1b,3] Second, especially for first-generation bioethanol, biofuels should ideally not be produced from food. Second-generation biofuels aim to resolve the issues of first-generation fuels by producing fully compatible fuels from sources that cannot be used for food such as nonedible vegetable oils, lignocellulosic material, and wastes.

Second-generation bio-fuels include fuels derived from non-edible vegetable oils or bio-oil derived from lignocellulosic material. This review concerns second-generation bio-fuels produced by thermal processes such as pyrolysis and liquefaction.

Compared to typical hydrocarbon fuels, both vegetable oil and bio-oil are poor selections as direct fuels owing to their high oxygen content, which leads to high viscosity, low volatility, corrosiveness, poor solubility in other hydrocarbons, and low energy content.^[3b,4] These oils tend to be hydrophilic, which can lead to high water contents and/or polymerization. Bio-oil, in particular, typically has an oxygen content within the 10–40 wt% range or even as high as 50 wt% and a water content of 15 to 30%.^[5] One solution to these oxygen-related problems is to perform deoxygenation with a heterogeneous catalyst similar to how petroleum oil undergoes desulfurization and denitrification by a hydrotreatment process. The main objective is to effectively remove oxygen in the form of CO_2 , CO , or H_2O .

Therein lies an issue—the use of H_2 , which is typically a major requirement for the deoxygenation of vegetable oils and bio-oils.^[1c,5b,6] However, there is a desire to reduce H_2 consumption and use systems that are either H_2 -modest (low H_2 pressures/flow rates) or use an inert atmosphere (no H_2).^[1b,c,6] The reason for this is because of the costs associated with the use of H_2 and the fact that the majority of the world's H_2 production comes from fossil-fuel reforming. Ideally, biofuels, which are supposed to be considered sustainable and renewable, should not be heavily dependent on nonrenewable sources.

Various reviews have been published in recent years with regard to the deoxygenation of biomass-derived bio-oils with focus on deoxygenation reaction pathways and hydrodeoxygenation processes in the presence of high-pressure H_2 , and therefore, they are out of the scope of this review. Gosselink et al.^[1b] review the deoxygenation of vegetable oils, fatty acid esters, and free fatty acids with a major focus on reaction pathways, especially in the presence of H_2 . Santillan-Jimenez and Crocker^[1c] focus primarily on reaction pathways for the deoxygenation of fatty acids under inert atmospheres. De et al.^[1a] provide an overview of recent work in the hydrodeoxygenation of bio-oil compounds derived from thermal processes. In their review of the general catalytic upgrading of bio-oil, Mortensen et al.^[5b] briefly cover hydrodeoxygenation processes of bio-oil. Reviews on the individual constituents that comprise bio-oil are also available, including one by Nakagawa et al.,^[7] who cover the upgrading of holocellulose-derived furanic compounds with a focus on general reaction pathways, and one by Bu et al.,^[8] who cover lignin-derived phenolic compounds.

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Despite the plethora of research that has been done within the past decade, there appears to be a lack of acknowledgement towards the development of catalysts for selectively deoxygenating bio-oils in H_2 -modest environments. Therefore, the purpose of this review is to summarize work that has been done in the development of the deoxygenation of vegetable oils and major bio-oil compounds (phenolic and furanic compounds) within H_2 -modest environments.

Herein, H_2 -modest environments are defined as having a severely reduced external supply of H_2 gas with pressures near atmospheric pressures, well below the typical minimum pressures required for hydrodeoxygenation processes. Emphasis and insight are provided for the development of catalysts that promote major reaction pathways that require low amounts of H_2 . It has been shown that traditional catalysts such as sulfide catalysts provide unfavorable results within these H_2 -modest systems. On the other hand, bimetallic catalysts containing an oxophilic metal and an active metal are shown to promote selective deoxygenation reactions that would prove beneficial in H_2 -modest systems. Finally, future research on catalytic deoxygenation by making use of internal hydrogen resources is also recommended.

Through thermodynamic calculations for deoxygenation reactions, several authors have demonstrated that equilibrium does not constrain these reactions, and thus, the reaction kinetics are deemed the constraining factor for product selectivity.^[1c,5b,9] The foremost decision in promoting selectivity is catalyst selection followed by optimization of the reaction conditions. Therefore, the study herein focuses primarily on the selection of an appropriate catalyst with recognition towards the impact of reaction conditions.

Kyle Rogers is a chemical engineering Ph.D. candidate and 2014 alumni of the University of New Brunswick. Kyle has been involved with the research and development of catalysts used for the deoxygenation of biomass-derived oils since 2012. His focuses are to make deoxygenation processes more economical and sustainable. Kyle is also the recipient of the 2014–2015 NBIF scholarship.



Professor Ying Zheng is the Canada Research Chair in Chemical Processes and Catalysis at the University of New Brunswick and the Chair of Chemical Reaction/Catalysis Engineering at the University of Edinburgh. Her research group focuses on synthesis of novel catalytic materials and the development of new catalytic processes to provide solutions to energy and environmental challenges.



2. Vegetable Oils/Triglycerides/Fatty Acids

The general deoxygenation of fatty acids and triglycerides from both edible and nonedible vegetable oils is widely discussed in the literature.^[1b,c,6,10] Reaction conditions that have typically been applied are temperatures of 230 to 375 °C and H_2 pressures of 10 to 110 bar (1 bar = 0.1 MPa); however, some researchers have begun to study the application of atmospheric or even inert atmospheres. Researchers have evaluated the processes by looking at various compounds and model oils such as the vegetable oils themselves, methyl and ethyl esters, and fatty acids. Vegetable oils are composed mostly of triglycerides and some free fatty acids. Triglycerides contain three fatty acids bound to a single propane unit through ester bonds (see Figure 1). Notably, all fatty acids have even-numbered carbon chains. Upon performing catalytic deoxygenation of vegetable oils, the main objective is typically to produce paraffins or olefins that may later undergo further processing into useful fuels.

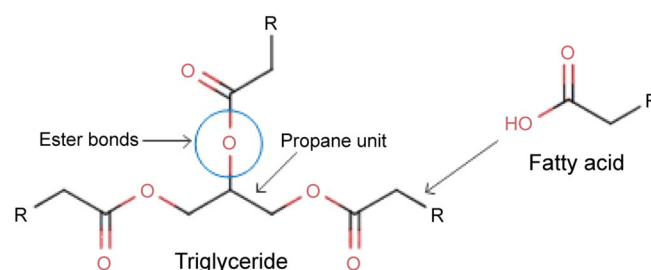


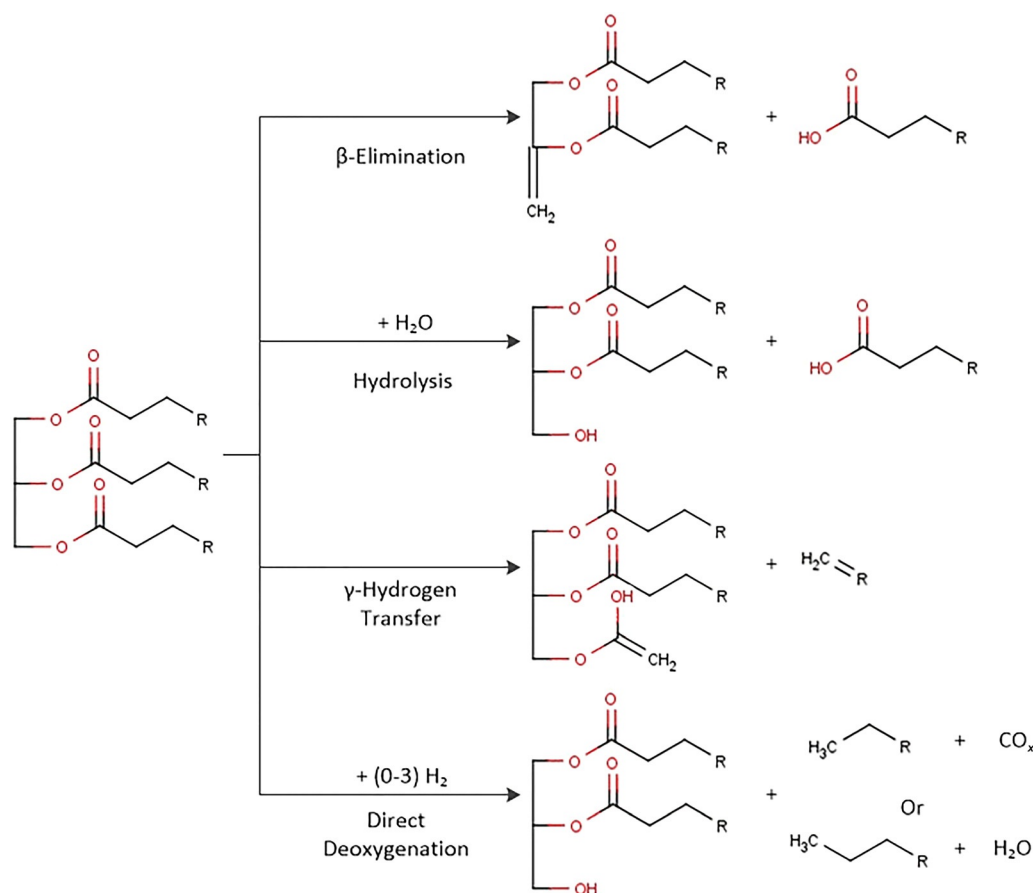
Figure 1. Structures of triglycerides and fatty acids.

2.1. Reaction mechanisms

2.1.1. Breakdown of triglycerides

Compared to deoxygenation reaction pathways for fatty acids, the reaction mechanisms by which the initial breakdown of triglycerides may occur have received far less attention and require additional research before they can be completely understood. Nonetheless, with vegetable oils as a feedstock, it is important to note how these reactions are dependent on reaction conditions, especially H_2 pressure.

It is often reported that during catalytic deoxygenation processes, the breakdown of triglycerides leads to the production of fatty acids and propane. Within the reaction conditions stated earlier for vegetable oils, the mechanism that is widely reported/accepted for the initial breakdown of triglycerides is termed β -elimination.^[1b,c,10m,t] The β -elimination mechanism starts off with the removal of one fatty acid unit, which leaves a glycol difatty ester unit (see Scheme 1).^[1c,10m] To remove the other fatty acids, the carbon double bond must be hydrogenated.^[10m] Therefore, under an inert atmosphere, triglycerides may produce fatty acid intermediates; however, conversion through β -elimination is limited to how much hydrogen is available on the catalyst surface or possibly produced by side reactions (e.g., dehydrogenation of fatty acid chains). Although many authors have accepted β -elimination as the primary reac-



Scheme 1. Initial break down of triglycerides.

tion mechanism for the breakdown of triglycerides, there is still a need for additional evidence to prove its operation.

Researchers have proposed other reaction mechanisms that may lead to the cleavage of triglycerides, including direct deoxygenation, γ -hydrogen transfer, and hydrolysis.^[1b,6,10m,r-t] Scheme 1 depicts all four major reaction mechanisms that have been proposed for the breakdown of triglycerides. Reports regarding γ -hydrogen transfer and direct deoxygenation reaction mechanisms under typical deoxygenation reaction conditions are very limited. Direct deoxygenation, characterized by a reaction in which the intermediates that are produced from the breakdown of the triglyceride remain adsorbed to the catalyst surface without a fatty acid intermediate, has yet to receive any quantifiable evidence as a major pathway.^[10r,s] To produce hydrocarbons at low H_2 consumption, the γ -hydrogen transfer mechanism does look promising; however, it is expected to be a more prevalent reaction mechanism for hydrocracking processes rather than for deoxygenation. This mechanism produces C_{n-2} hydrocarbons from the original fatty acid carbon chains at temperatures of approximately 450°C as opposed to the typical deoxygenation reaction temperature range of 230 to 375°C .^[1b,10m] At such a temperature, cracking of the hydrocarbon chains should be anticipated.^[11]

The hydrolysis reaction route successfully produces fatty acids and produces 1 mol of glycerol rather than propane.^[6,12] It has been reported as a potential reaction step in the deoxy-

genation reaction process. For example, Şenol et al.^[13] suggest that during the deoxygenation of methyl hexanoate within a temperature range of 250 to 300°C at 1.5 MPa, the methyl ester may undergo de-esterification through a hydrolysis reaction over sulfided catalysts supported on $\gamma\text{-Al}_2\text{O}_3$. Gosselink et al.^[1b] suggest that this may also be applicable to triglycerides. Hollak et al.^[12b] further demonstrated the hydrothermal deoxygenation of triglycerides first by the hydrolysis of triglycerides followed by the deoxygenation of the resulting fatty acids at 250°C without H_2 over a Pd/C catalyst. Unfortunately, high yields of deoxygenated hydrocarbons could not be attained.

For typical deoxygenation processes, β -elimination still remains the most predominant reaction mechanism that has been reported for the breakdown of triglycerides during catalytic deoxygenation.^[1b,c,10t] The reliance on β -elimination is an issue in terms of catalytic deoxygenation without a source of hydrogen molecules, as hydrogen is required at least to some extent to remove all three fatty acids successfully. It is definitely possible to remove oxygen from fatty acids without H_2 present, as will be discussed below. As a result, it has been claimed that, in a H_2 -modest system, the rate-determining step for the deoxygenation of vegetable oils is the β -elimination reactions.^[10f] Therefore, to develop viable processes for deoxygenating vegetable oils under low- H_2 atmospheres or even under inert atmospheres, the challenge is either to promote one of

the other reaction mechanisms, such as hydrolysis, or to change the source of hydrogen.

2.1.2. Deoxygenation of fatty acids

Oxygen can be removed from fatty acids to produce alkanes/alkenes by three main reaction pathways: hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO_2). These reaction pathways are represented in Scheme 2. The HDO pathway, which consumes the highest amount of H_2 , is an overall exothermic reaction process that removes oxygen as water through a series of hydrogenation and hydrogenolysis reactions. DCO removes oxygen as both water and CO to produce alkanes/alkenes with one less carbon atom than the precursor fatty acid with the consumption of 0–1 mol H_2 per mol of fatty acid, depending on the reaction mechanism, which will be discussed below in greater detail. DCO_2 releases oxygen as CO_2 and produces alkanes with one less carbon unit. DCO_2 effectively consumes no H_2 and has actually been shown to be inhibited by H_2 pressures that are too high.^[10e,q] Unlike the HDO reaction pathway, the DCO_x reaction pathways are overall endothermic reactions and generally favor increasing reaction temperatures, whereas HDO reactions may experience a decline in selectivity.^[9,14]

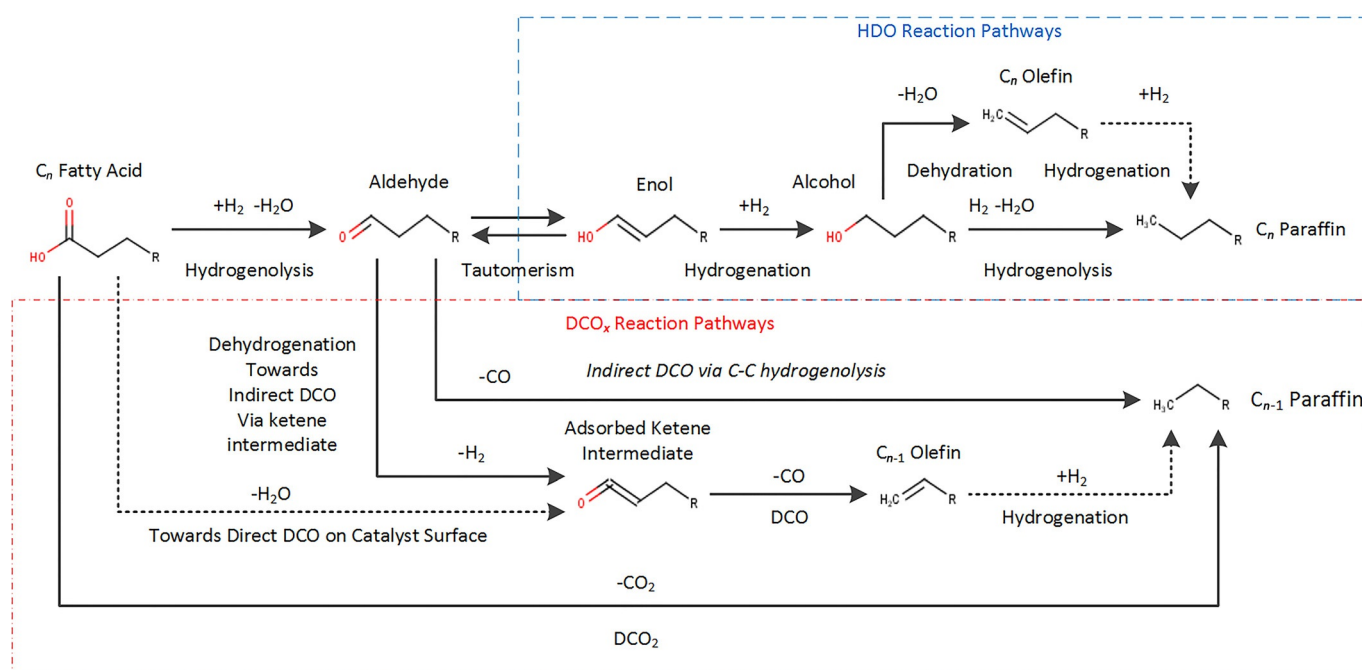
2.1.2.1. Primary deoxygenation reactions

As seen in Scheme 2, fatty acids have three initial reaction pathways that can lead to the removal of oxygen. One pathway is the removal of the hydroxy group as H_2O through a hydrogenolysis reaction mechanism involving dehydration and hydrogenation reactions. The removal of the hydroxy group by the first pathway is reported to lead to an adsorbed aldehyde

intermediate.^[10i–k] However, the organic species may stay bound to the catalyst and directly undergo subsequent reactions rather than being desorbed as an aldehyde compound. This can potentially result in the “direct DCO” reaction pathway if the adsorbed intermediate undergoes C–C scission. The third possible reaction pathway for initial deoxygenation is DCO_2 .

The actual mechanisms for DCO_2 and direct DCO are not completely understood, and additional research is required to verify the mechanisms that have been proposed. Currently, there are three major reaction mechanisms to consider. The first mechanism involves first dehydrogenation of the fatty acid to lead to a strongly bound organic compound that, after C–C scission, would have to undergo hydrogenation for it to be desorbed.^[10e] This mechanism has been explored in great detail by Lu et al.,^[10e] who have researched the DCO_x reaction mechanisms of carboxylic acids (propionic acid) on a Pd(111) model surface at various H_2 partial pressures: 0.01, 1, and 30 bar.

At all pressures, the DCO_2 reaction pathway begins with the partial dehydrogenation of the α -carbon atom followed by dehydrogenation of the hydroxy group, and then total dehydrogenation of the α -carbon atom, which leads to a strongly adsorbed organic compound. Scission of the C–C bond releases CO_2 . Before the product may be released, it must undergo hydrogenation and hydrogen transfer to produce either an alkene or an alkane.^[10e] The direct DCO reaction mechanism begins with the partial dehydrogenation of the α -carbon atom. In a very low H_2 environment (0.01 bar), this step is followed by dehydrogenation of the β -carbon atom and then removal of the –OH group. At higher H_2 partial pressures, the previous two steps proceed in the reverse order. Prior to C–C scission, which releases CO, the β -carbon atom is once again dehydrogenated. A final alkene or alkane product is released upon hy-



Scheme 2. Deoxygenation pathways of fatty acids.

drogenation of the carbon pool.^[10e] Overall, the direct DCO route is more kinetically favorable; however, both reaction pathways suffer upon increasing the H₂ pressure. It is also important to note that the rehydrogenation of the carbon pool is one of the rate-limiting steps in the mechanism. This suggests that it is important that the catalyst maintains surface hydrogen in the proximity of the adsorbed carbon pool; otherwise, these reaction mechanisms pose a risk of catalyst coking.

The other possible mechanisms for direct DCO_x include the production of formic acid as an intermediate and ketonization.^[10p,u-w] It has also been proposed that DCO₂ occurs through the formation of formic acid, which readily decomposes into CO₂ and H₂.^[10p,u,v] The H₂ that is produced would then be consumed for hydrogenation of the resulting C=C bond. Alternatively though, formic acid may decompose into CO and H₂O, which would be favored in H₂-containing environments.^[10w] Although there is a lack of quantifiable evidence to support this mechanism as a result of the rapid decomposition of formic acid, this mechanism cannot be ruled out and should receive consideration.^[10j] Another reaction mechanism that has been postulated for the removal of oxygen from fatty acids is ketonization with subsequent deoxygenation.^[10a,i,m] This reaction mechanism, however, has not been widely discussed and is not as widely accepted as the C–C scission and formic acid mechanisms.

2.1.2.2. Secondary deoxygenation reactions

If hydrogenolysis occurs as the primary deoxygenation reaction, which produces an aldehyde intermediate, then secondary deoxygenation reactions are required to remove the remaining oxygen atom. The aldehyde intermediate may undergo indirect DCO or subsequent HDO reactions (see Scheme 2).

For indirect DCO, two mechanisms have been proposed, both of which start with an adsorbed alkanoyl structure. One such reaction mechanism resembles the direct DCO mechanism described by Lu et al.,^[10e] in which the aldehyde forms a ketene intermediate on the catalyst surface.^[10k] Ruinart de Brimont et al.^[10k] suggest that this mechanism is favorable if the alkanoyl species is in close proximity to another organic species that requires hydrogen for its reaction, such as the hydrogenolysis of an adjacent fatty acid. The presence of a ketene structure on the catalyst surface has been confirmed by Peng et al.,^[10i] however, they propose that it is part of a ketonization reaction pathway that leads to DCO₂. This mechanism could produce an alkene at an overall consumption of no H₂ from fatty acid to alkene.

The second reaction mechanism that has been proposed for indirect DCO involves a hydrogenolysis reaction.^[10a,i] This reaction route uses surface hydrogen to break the C–CO bond to produce an alkane and CO.^[10i,k] Starting from a fatty acid to the production of the alkane unit, this reaction pathway consumes 1 mol of H₂. Given that the alkene and alkane produced from either indirect DCO reaction pathway may be produced from each other through hydrogenation/dehydrogenation and the fact that hydrogen is involved in both reaction pathways, it is

difficult to distinguish between the two without performing an in-depth mechanism study on a per catalyst basis.

Alternatively, the adsorbed aldehyde species may not undergo DCO and may instead follow the HDO route, through which it is hydrogenated to an alcohol; this alcohol may then undergo dehydration/hydrogenolysis. This route is undesired, as it would require an additional 2 mol of H₂ to produce an alkane or an additional 1 mol if dehydration of the alcohol is favored to produce an alkene. It has been proposed that the aldehyde and alcohol products are in hydrogenation/dehydrogenation equilibrium owing to keto–enol tautomerism.^[10i] Removal of the hydroxy group is considered the final step of the HDO reaction pathway and is thought to be rate determining.^[10i,j] In a H₂-modest system, this reaction is not expected to significantly occur owing to the fact that 3 mol of H₂ are required to produce an alkane from a fatty acid. In this regard, the indirect DCO reaction route is more desirable, as it requires less H₂, and as H₂O and CO are both produced from this pathway, there is the possibility to reproduce any H₂ that is consumed (see Section 5.3.).

2.1.2.3. Side reactions and pathway selection

Throughout the reaction pathways that have been mentioned, other reactions, such as hydrogenation or the reverse reaction, dehydrogenation, are possible, depending on the reaction conditions such as H₂ pressure and temperature. If little-to-no H₂ is available, it is expected that dehydrogenation reactions will occur. Excessive dehydrogenation can lead to the formation of aromatic structures.^[9] Other side reactions that must be considered are cracking reactions, which can produce shorter hydrocarbon chains (such as C₄–C₁₀) from long paraffinic products such as hexadecane or even fatty acids at elevated temperatures $\geq 300^\circ\text{C}$.^[9,10b,c,x,15]

The DCO₂ and DCO reaction routes are claimed to be the more appealing reaction routes, as they require fewer activated hydrogen sites and thus less H₂.^[1c] As DCO_x reactions are related to cracking reactions, they have been shown to be the most prevalent at elevated temperatures (typically $> 300^\circ\text{C}$) owing to their endothermicity.^[6,9,10d,o,15,16]

2.2. Catalyst selection

Although many studies have been performed for the general deoxygenation of vegetable oils and fatty acids, these studies appear to be mostly limited to the application of certain catalysts. These include conventional sulfide catalysts that are used for desulfurization/denitrification in the petroleum industry, that is, supported CoMoS and NiMoS catalysts, and monometallic metal catalysts, specifically Ni, Pt, and Pd. Compared to studies performed with phenolic and furanic compounds, the development of bimetallic catalysts has received very little attention for deoxygenating vegetable oils. The potential for using bimetallic catalysts with vegetable oils is discussed in Section 5.2.

2.2.1. Active material

2.2.1.1. Sulfide catalysts

In general, sulfided NiMo and CoMo catalysts are regarded as not being active within a H₂-free environment.^[1b] Although the selectivity of sulfide catalysts may be promoted toward DCO_x reactions by a second metal such as Ni or simply by elevating the temperature (>350 °C), these catalysts are overall reported as being most active towards the HDO reaction route and rely heavily on H₂.^[10d,o,p,14] Reports state, however, that decreasing the H₂ pressure over a sulfide catalyst increases the selectivity towards DCO_x reactions often at the cost of the overall yield of the desirable products.^[10d,o,p,15,17] However, the conversion of fatty acids decreases if this occurs.^[15] Therefore, it can be theorized that the selectivity toward DCO_x reactions increases, because the reaction rate of the HDO route drops, which allows the DCO_x reactions to be more competitive.

Sulfide catalysts are inappropriate for a H₂-modest system to perform the deoxygenation of fatty acids. There are two reasons for this: the lack of activity towards DCO_x and deactivation issues. During the hydrotreatment of vegetable oils/fatty acids, sulfide catalysts become deactivated because of the removal of sulfur from the surface as a result of oxidation and coking.^[10o,18] Therefore, to maintain catalyst activity, a sulfur source such as H₂S must be fed into the system to replenish the sulfur sites on the catalyst. This is a drawback for these catalysts with respect to environmental issues.^[1b,c] In addition, maintaining activity is difficult, as some degradation of the sulfur sites is irreversible.^[18a]

2.2.1.2. Monometallic catalysts

Monometallic transition-metal catalysts are becoming very common for the deoxygenation of fatty acid/triglycerides. The most commonly researched catalysts are Ni and the noble metals Pt and Pd. In general, these catalysts are selective towards DCO_x reactions.^[6,9,10c,g,i,n,19] Snåre et al.^[9] have screened various catalysts for their activity towards DCO_x reactions at 300 °C with a He pressure of pressure of 6 bar. They have determined that the reactivities of the catalysts follow the order Pd > Pt > Ni > Rh > Ir > Ru > Os.^[9]

Monometallic catalysts have been tested in both H₂-rich and inert/low-H₂ environments. Rozmyslowicz et al.^[10j] demonstrate in both a H₂-rich and a H₂-free environment that Pd is selective towards DCO_x. In comparison though, reactions under an inert atmosphere are far less active, as the yield of hydrocarbons is 36% less than that obtained in the H₂-rich environment. Hengst et al.^[10c] report that upon treating oleic acid in a H₂ environment, adding 0.5 wt% Pd to a γ-Al₂O₃ support increases the conversion and C₁₇ selectivity from 50% at 0% selectivity (without the addition of Pd) to 90% at 30% selectivity. Increasing the Pd content further to 2 wt% increases the conversion to 99% and increases the C₁₇ selectivity to 47 wt%.^[10c] In conjunction, Alotaibi, et al.^[10a] report that DCO_x only occurs on Pt and Pd catalysts under a H₂ atmosphere. The higher dependence on H₂ reported by Alotaibi et al.^[10a] may be due to the use of an acidic salt, Cs_{2.5}H_{0.5}PW₁₂O₄₀, as a support.

Peng et al.^[10i] report that although a Ni catalyst (supported on ZrO₂) favors DCO_x reactions for the deoxygenation of palmitic acid under 12 bar H₂ at 260 °C with a selectivity towards pentadecane of 90% and an overall conversion of 100%, changing to an inert N₂ atmosphere decreases the selectivity to 16% at a conversion of 3.5%. Therefore, they conclude that even though monometallic catalysts favor DCO_x reactions, a source for disassociated hydrogen protons on the catalyst surface is still required to provide adequate results. The optimum amount of H₂ required is yet to be determined.

In Section 2.1., it is suggested that direct DCO_x reactions diminish upon increasing the H₂ pressures, as demonstrated by Lu et al.^[10e] for a microkinetic model on a Pd(111) surface. Given that Pd and Pt catalysts persevere in H₂ environments, it is likely that, as Peng et al.^[10i] suggest for their Ni catalyst, the Pd and Pt catalysts follow an indirect DCO route, which is faster than the direct DCO_x reaction in the presence of H₂.^[10a,i,j]

One well-known issue with monometallic transition metals used for the deoxygenation of fatty acids is catalyst deactivation. Severe deactivation is reported for catalysts under inert atmospheres.^[9,10b,20] For example, Bernas et al.^[10b] report that within 28 h of treating dodecanoic acid under an argon atmosphere at 300 °C the activity of their 1% Pt/Sibunit catalyst decreases significantly as the conversion drops from 85 to 3%. They claim that deactivation is due to coking.^[10b] This may be explained by the reaction mechanisms described by Lu et al.,^[10e] who conclude that one of the rate-limiting steps in DCO₂ and direct DCO is the hydrogenation of the hydrocarbon pool. A catalyst's inability to hydrogenate the hydrocarbon pool would effectively lead to carbon deposition.

On the basis of the literature, it is concluded that transition-metal catalysts are appropriate for the deoxygenation of fatty acid containing oils within a H₂-modest system, especially if they are compared to sulfide catalysts. Two issues that are worth considering though are cost and deactivation. Owing to the high costs associated with noble-metal catalysts, it is recommended that work be done to develop catalysts that are equally active yet more cost effective. It is claimed that Ni catalysts with an increased metal content can achieve results comparable to those of noble catalysts.^[10t] To further promote selective deoxygenation with minimal hydrogenation activity, researchers are advised to study the deoxygenation of triglycerides with catalysts that are developed for phenolic and furanic compounds, such as bimetallic catalysts. Processes that are completely H₂ free do not appear to be viable as a result of reduced activity, increased deactivation, and the fact that complete conversion of triglycerides is difficult because of limitations in terms of β-elimination reactions. Therefore, a low-H₂-containing environment should be used with a catalyst that is able to maintain high activity.

2.2.2. Catalyst support

Catalyst supports that have been widely used by researchers include carbonaceous (for noble-metal catalysts in particular) and SiO₂ supports, as these supports are generally inert towards deoxygenation. Many studies report the use of alumina

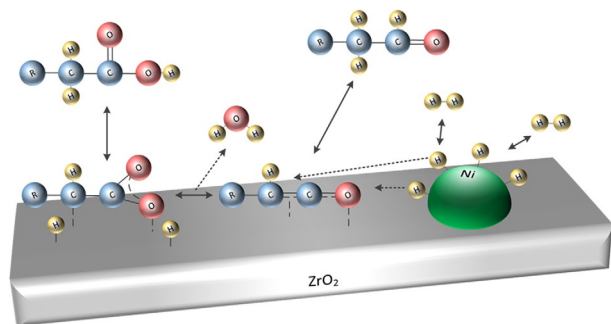
and zeolites as supporting materials, as they are conventional supports used in the hydroprocessing of petroleum fuels. An ideal support should be one that works in tandem/synergy with the active material.

The acidity of a catalyst can impact its activity by providing additional reaction sites that may be used for H_2 disassociation or adsorption of the oxygenated compounds. Some supporting materials such as zeolites and alumina are regarded as acidic supports and, especially for the case of zeolites, contain an abundance of Brønsted acid sites (alumina supports tend to consist of more Lewis acid sites).^[1b,10]

Brønsted acid sites promote sequential hydrogenation–dehydration–hydrogenation reaction routes, which would favor HDO reaction pathways.^[10i,21] However, the presence of strong acid sites, such as those found on zeolites, have been shown to be prone to rapid deactivation owing to coke deposits.^[10c]

Lewis acid sites, on the other hand, promote indirect DCO reactions.^[10i,22] Addition of appropriate Lewis acidity to a catalyst may be considered to enhance selective deoxygenation. Peng et al.^[10] demonstrate for the deoxygenation of palmitic acid at 260 °C with 12 bar H_2 that by switching from Pt and Pd supported on C to ZrO_2 increases the conversion from 20–30% to >98%. Although the DCO_x selectivity on the Pt catalyst decreases from 98 to 61%, the selectivity towards DCO_x on the Pd catalyst is maintained at 98%. In addition, Ni/ ZrO_2 favors DCO_x with a selectivity of 90% at a conversion of approximately 100%. It is concluded that the ZrO_2 support shifts the reaction pathway from direct DCO to indirect DCO.^[10]

Reducible oxide supports containing Lewis acid sites such as ZrO_2 , TiO_2 , CeO_2 , and Cr_2O_3 are able to reduce carboxylic acids to aldehydes selectively.^[10] These supports adsorb the oxygenated compounds through oxygen vacancies. It is proposed that this occurs through the abstraction of the hydrogen atom from the –OH group and an α -hydrogen atom to produce water and a ketene intermediate.^[10] It is proposed that the said intermediate is hydrogenated to produce an aldehyde by Ni and that it eventually undergoes decarbonylation.^[10] As such, the active metal behaves synergistically with the supporting material (see Scheme 3). Therefore, the presence of a reducing agent such as H_2 remains important for reducible oxide supports, as without it, these supports cannot maintain activity.



Scheme 3. Synergism of Ni and ZrO_2 .^[11]

A novel approach to the development of reducible oxide supports is demonstrated by Shim et al.,^[10] who have studied a combination of CeO_2 and ZrO_2 (produced by the coprecipitation of zirconyl nitrate and cerium nitrate) for the deoxygenation of oleic acid to exploit the nature of these materials to store oxygen, especially CeO_2 , and to develop a catalytic support material with improved redox properties and thermal resistance. Reaction studies show that $Ce_{0.6}Zr_{0.4}O_2$ alone has an oxygen removal efficiency of 32.2% and is selective towards DCO_x reactions upon treating oleic acid with 1 atm mixture of 20% H_2 in N_2 .^[10] The reactivity is attributed to the cubic phase of the material, as it has a higher capability of producing a redox couple between Ce^{4+} and Ce^{3+} . The $Ce_{0.6}Zr_{0.4}O_2$ material is also noted to promote cracking reactions, so the contact time should be minimized.^[10]

If a H_2 -free system is applied to deoxygenate fatty-acid-containing oils, it is advised that the selected catalyst support be inert by nature, such as carbon or SiO_2 . Reducible oxide catalyst supports are unsuitable for a H_2 -free environment, as they require H_2 for activation. If, however, a low- H_2 -containing environment is desired, such as that described in the previous section, the selection of a reducible oxide material as a support may be suitable, as they have synergistic effects with relevant catalysts such as Ni that improve the overall activity and selectivity towards desirable DCO reactions.

3. Phenolic Compounds

As research into the possible applications of bio-oil developed by thermal processing of lignocellulosic material is becoming more extensive, work is being done to understand and develop processes for the catalytic deoxygenation of said bio-oil. Bio-oil tends to be a very complex mixture of various oxygenated compounds owing to the various breakdown reactions of cellulose, hemicellulose, and especially lignin, which, of course, are dependent on processing conditions and the original feed. In excess of 300 different compounds have been identified in bio-oil.^[23] Of these compounds, phenolic compounds, derived from lignin, are prevalent. Most phenolic compounds that are present are either alkyl-substituted phenols, such as cresol, or methoxy-substituted phenols, such as guaiacol (see Figure 2 for examples of phenolic compounds).^[8]

Relative to fatty acids, phenolic compounds are considered to be more difficult to deoxygenate because of the aromatic structure. A major challenge for developing deoxygenation process for phenolic compounds is the development of catalysts that can perform deoxygenation without saturating the aromatic rings so as to minimize the consumption of H_2 .^[1a,8]

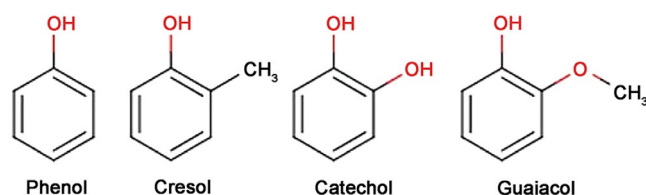


Figure 2. Structures of example phenolic compounds.

3.1. Reaction mechanisms

The actual reaction mechanisms for compounds such as phenol, cresol, and guaiacol have received little attention. However, simply on the basis of the structures of such compounds, it can be clearly gathered that H_2 is required to remove oxygen as water. Unlike fatty acids, oxygen cannot be removed in the form of CO or CO_2 ; therefore, deoxygenation will not occur without a source of hydrogen atoms. Work has been done though to develop catalysts that minimize H_2 consumption by selectively using H_2 to remove oxygen and not to saturate the aromatic ring.^[24]

3.1.1. General deoxygenation reaction pathways

There are two overall reaction pathways that may be followed for deoxygenation of phenolic compounds. The first reaction route involves the complete saturation of the aromatic ring followed by cleavage of the C–O bond likely through dehydration to generate a C=C bond that is to be hydrogenated again.^[1a,8] This exothermic reaction pathway is often referred to as the “hydrogenation (HYD) route”. The second reaction route is known as the direct deoxygenation (DDO) route and involves a hydrogenolysis reaction to break the C–O bond selectively while keeping the aromatic structure (see Scheme 4).^[8,24a] The actual catalytic mechanism for this hydrogenolysis reaction is not fully understood and requires additional research. Although both reaction pathways are exothermic, Mortensen et al.^[5b] report that the thermodynamic equilibrium will not have a major hindrance on the reactions at temperatures below 600 °C.

The selectivity of DDO reactions over HYD appears to be very dependent on the properties of the catalyst. DDO seems to be dependent on the catalysts ability to adsorb oxygen through the use of oxygen vacant sites or the use of an oxophilic metal. Phenolic compounds adsorb primarily through the hydroxy groups by weak interactions with the aromatic ring.^[24a,25] In contrast, catalysts that favor HYD reactions tend not to possess any Lewis acid sites, and adsorption occurs through the aromatic ring.^[5a,25b,26] These catalysts suffer the inability to surpass the reaction energy barrier required to

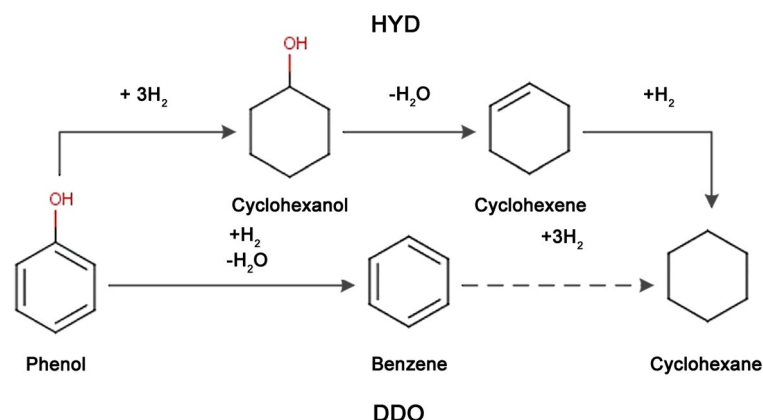
remove oxygen directly from the ring structure and must saturate the ring first to lower the energy barrier.

3.1.2. Deoxygenation of substituted phenolic compounds

Substituted, *ortho*-substituted, phenolic compounds are more difficult to deoxygenate owing to steric hindrance.^[5b,27] Guaiacol is a typical example because of the *ortho*-substituted methoxy group that requires deoxygenation as well. The catalytic reaction mechanisms for removing the methoxy group of guaiacol and similar compounds have not been widely discussed and warrant future investigations. A hydrogenolysis reaction could break the C–O bond either at the site of the aromatic ring to produce methanol [i.e., demethoxylation (DMO)] or at the methyl group to produce methane [i.e., demethylation (DME)] whilst leaving a hydroxy group that may undergo subsequent removal from the aromatic ring.^[24b,c,28] For example, Bui et al.^[24c] note that both catechol and phenol are the major products from the catalytic deoxygenation of guaiacol. The production of catechol in significant amounts from guaiacol has also been witnessed by Zhao et al.^[24e]

On the contrary, Prasomsri et al.^[24a] witness transalkylation reactions of methoxy groups during the deoxygenation of anisole.^[24a] This, therefore, demonstrates that in addition to the DMO and DME reaction routes, methoxy groups may also undergo transalkylation reactions. This has also been demonstrated by Runnebaum et al.,^[29] who suggested that the transalkylation is due to acidic sites on the catalyst support. Scheme 5 depicts the general reactions related to the deoxygenation of phenolic compounds containing methoxy groups such as guaiacol.

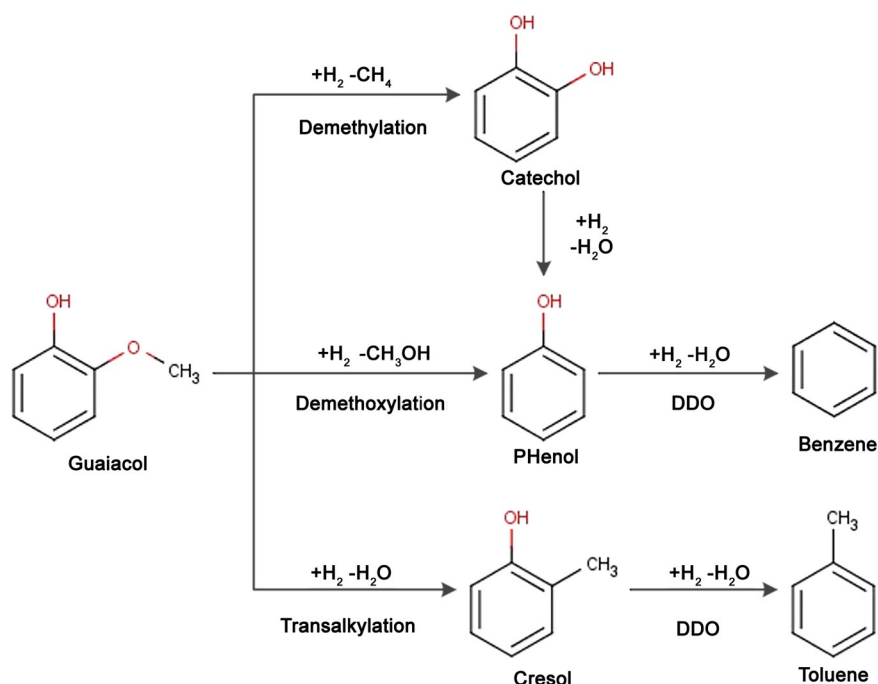
One major consideration that must be made upon deoxygenating phenolic compounds is that, owing to fuel regulations, producing benzene is not favorable if the product is to be potentially used in the fuel market. Therefore, focus should be applied to maintaining or possibly adding methyl groups to the aromatic structure. One example would be to attempt to develop a catalyst that is both selective towards the DDO of hydroxy groups and selective towards the transalkylation of methoxy groups.



Scheme 4. DDO and HYD reaction pathways for the conversion of phenol.

3.2. Catalyst selection

Although studies regarding the reaction mechanisms of phenolic compounds are lacking, there appears to be a lot of research work done in the development of catalysts, especially those that promote high levels of deoxygenation while minimizing H_2 consumption by ring-saturation and ring-opening reactions. In comparison to work being done with triglycerides/fatty acids, a larger variety of catalysts are being developed for the deoxygenation of phenolic compounds. Catalysts that have received attention include conventional metal sulfides, metal oxides, transition metals, transition-metal phosphides, metal carbides, and bimetallic catalysts.



Scheme 5. General conversion scheme of guaiacol.

3.2.1. Active material

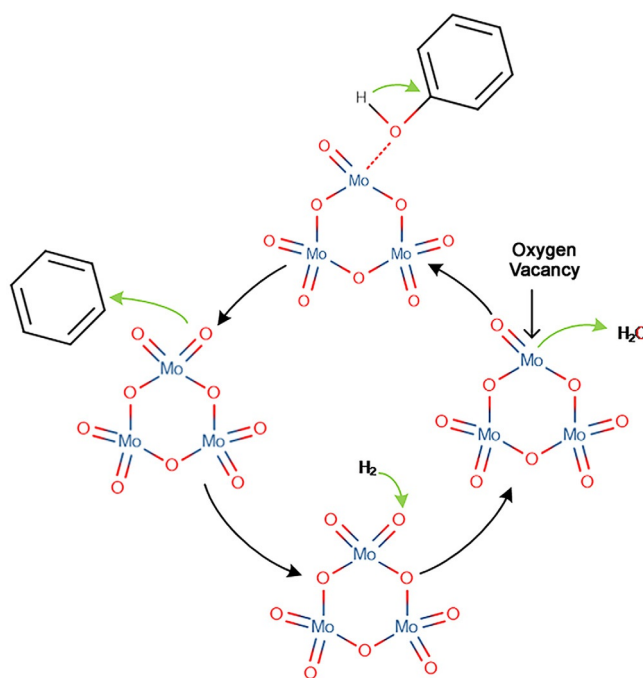
3.2.1.1. Sulfide catalysts

Relative to fatty acids, metal-sulfide catalysts have received far less attention. Although promoted MoS_2 , sulfide catalysts, in general, support the HYD reaction route.^[24b,30] On the contrary, relative to noble-metal catalysts, sulfide catalysts produce more DDO reaction pathway products.^[31] On the other hand, deactivation of sulfide catalysts during deoxygenation of bio-oils is a widely studied topic. Similar to vegetable oils, a sulfur source must be added to the bio-oil to maintain activity, which likewise is unfavorable.^[5b,32] The major issue is in regard to the high water content of bio-oil, which can rapidly oxidize and deactivate sulfide catalysts by replacing sulfur and/or by producing a sulfate phase that blocks the active sites.^[32b,33] At elevated reaction temperatures, sulfide catalysts have also been shown to deactivate as a result of coking.^[32a,b] Notably, in comparison to other catalysts, sulfide catalysts have received more attention in terms of deactivation and are, therefore, considered more mature.

3.2.1.2. Metal-oxide catalysts

Metal-oxide catalysts, on the other hand, have received much attention. It is proposed that, owing to oxygen vacancies, which act as acid sites, some metal-oxide catalysts may be selective towards DDO.^[5b,24a,34] This has been demonstrated by Prasomsri et al.,^[24a] who have used a MoO_3 catalyst to deoxygenate various model compounds for biomass-derived oxygenates.^[24a] They show that aromatic oxygenates can be successfully converted into oxygen-free aromatics, which confirms

that the catalyst promotes that DDO reaction pathway. As for deactivation; the catalyst may be regenerated by a simple calcination procedure. It is suggested that the H_2 pressure should be increased to prevent water from blocking the active sites; however, this would not be viable for systems in which the attempt is actually to minimize H_2 consumption.^[24a] See Scheme 6 for the general deoxygenation mechanism of MoO_3 . On the basis of the results obtained by Whiffen and Smith,^[35]



Scheme 6. General deoxygenation mechanism of MoO_3 .^[25a]

who found MoO_3 to be less active than MoS_2 , Mortensen et al.^[5b] suggest that WO_3 may be a more suitable catalyst than MoO_3 .

3.2.1.3. Metal-phosphide catalysts

An interesting new type of catalyst that has been proposed for the catalytic deoxygenation of bio-oil compounds is transition-metal phosphides. Zhao et al.^[24e] propose the use of transition-metal phosphide catalysts for the catalytic deoxygenation of guaiacol.

After testing a variety of transition-metal phosphide catalysts supported on SiO_2 , Ni_2P was found to be the most active and stable. At 300 °C and atmospheric pressure, the Ni_2P catalyst is selective towards the production of benzene with a selectivity of approximately 60% at a conversion of 80%.^[24e] In later work, the same research group proposes that transition-metal phosphide catalysts, such as Ni_2P , are comparable to noble-metal catalysts based on acidic supports because they are bi-functional and display both acidic and metallic properties.^[36] In addition, these catalysts (Ni_2P in particular) are resistant to deactivation. It is suggested that Ni_2P , for example, has an excess amount of phosphorus in the form of phosphate species on the surface, and these species interact with water effectively to prevent the oxidation of the Ni_2P particles.^[36]

3.2.1.4. Metal-carbide catalysts

In contrast to sulfide, oxide and phosphide catalysts, attention has also been focused on metal-carbide catalysts, most specifically tungsten and molybdenum carbides. The purpose for their development was potentially to produce cost-effective catalysts that behave in a manner similar to that of noble metals.^[37] These catalysts are typically supported on carbon supports to eliminate the need for methane for carburization.^[37,38] Boullosa-Eiras et al.^[39] compare Mo_2C to oxide, phosphide, and nitride catalysts for the deoxygenation of phenol. The trend in activity (based on conversion) that they establish is $\text{Mo}_2\text{C} > \text{MoO}_3 > \text{Mo}_2\text{N} > \text{MoP}$. All catalysts are most selective towards DDO reactions; however, the phosphide catalyst experiences more hydrogenation reactions.^[39]

Jongerius et al.^[38] study the use of W_2C and Mo_2C catalysts at 55 bar H_2 within a temperature range of 300 to 375 °C for the deoxygenation of guaiacol. They report that the catalysts are mostly selective towards the production of phenol by demethoxylation with very few ring-saturation reactions. This is also demonstrated by Ma et al.^[40] and Santillan-Jimenez, et al.^[37] Overall, Jongerius et al.^[38] demonstrate that Mo_2C is more active and stable than W_2C , which deactivates quickly as a result of oxidation and an increase in particle size.^[38] Both catalysts experience difficulties in regaining activity with reactivation (by recarburization); the Mo_2C catalyst, for example, experience a decrease in the conversion from 68 to 51% if the catalyst is recycled and recarburized between two consecutive runs.^[38] This is attributed to the possible encapsulation of the carbide particles within the support or irreversible coke formation, as confirmed by Santillan-Jimenez et al.^[37]

Although carbide catalysts appear to favor reaction routes that do not involve ring saturation, which thereby reduces H_2 consumption, they may be considered unsuitable for extended use. This is because the carburization process requires extremely high temperatures (1000 °C), and once deactivated, the catalysts cannot be successfully regenerated.

3.2.1.5. Monometallic catalysts

Transition metals (noble metals in particular) have attained some interest in the deoxygenation of phenolic compounds because of the fact that they are able to activate H_2 . Noble metals have been demonstrated to be able to achieve higher degrees of deoxygenation than commercial sulfide catalysts.^[26] However, these catalysts have been shown to require high H_2 pressures. As demonstrated by French et al.,^[5a] who have tested noble-metals catalysts (Pt, Pd, and Ru) and compared them to a conventional sulfide NiMo catalyst under H_2 pressures of 70–170 bar, even at such high H_2 pressures, oxygenated aromatic compounds are in the products. Increasing the temperature from 340 to 400 °C increases the conversion of phenolic compounds into aromatics and cycloalkanes. Although the Pt catalyst is the only catalyst to decrease coking with an increase in temperature, the yield of the deoxygenated liquid products is lower than that obtained with the conventional NiMoS catalyst.^[5a] The Pd catalyst, on the other hand, favors ring saturation over deoxygenation reactions, which demonstrates high H_2 consumption. Nie and Resasco^[41] also report that Pt favors ring-saturation reactions; however, they propose that the catalyst offers a variation of the HYD reaction mechanism, in which a cyclic ketone is formed (by keto–enol tautomerism) and is then hydrogenated.

In summary, monometallic catalysts such as Ni, Co, Pt, and Pd are not ideal catalysts because of their high H_2 requirements and the fact that they generally favor ring-saturation reactions over DDO.^[25b,26,41,42]

3.2.1.6. Bimetallic catalysts

The use of bimetallic catalysts for the deoxygenation of both phenolic and furanic compounds has received much attention in recent years. The purpose for their development was to improve the activity of monometallic catalysts towards DDO reaction pathways over HYD and ring-opening reactions and to increase catalyst stability.^[25b,43] Alonso et al.^[43] review a variety of bimetallic catalysts that have been developed for various intentions and discuss how the addition of a second metal may affect the catalyst overall. Within the past three years, many researchers have focused on the combination of active metals such as Pt, Pd, and Ni with other metals that are typically less active for deoxygenation such as Co, Cu, Fe, and Sn.^[25,44] The general consensus is that the addition of the secondary metals alters the catalyst selectivity from promoting HYD reaction routes to promoting DDO reaction routes.

One bimetallic catalyst that has received attention is the addition of Cu to Ni for a NiCu bimetallic catalyst. Zhang, et al.^[44g] report the addition of 5 and 15 wt% Cu to a 10 wt% Ni cata-

lyst for the deoxygenation of guaiacol. The addition of 5 wt% Cu to a Ni catalyst decreases the selectivity towards cyclohexane from 97.0 to 80.8%. These decreases are balanced by increases in selectivity towards benzene and toluene, which demonstrates that the addition of Cu promotes transalkylation reactions. Increasing the Cu content further to 15 wt% decreases the cyclohexane selectivity to 60.1%; however, the conversion also decreases.^[44g]

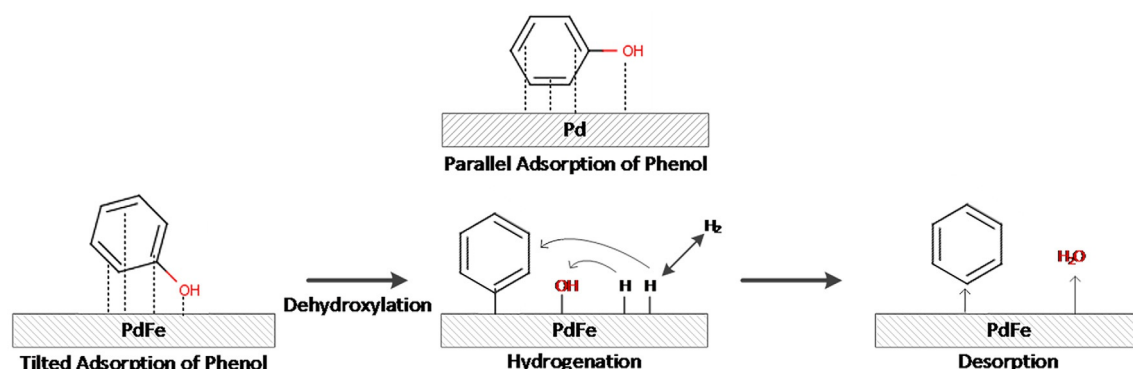
Huynh et al.^[44e] have further studied the substitution of Ni with Cu on a 19 wt% Ni/HZSM-5 catalyst to improve the reducibility of Ni. Rather than alloying with Ni, Cu forms as a separate layer with large particle sizes. The substitution of 2 wt% Ni with Cu decreases the conversion of phenol from 98 to 50%.^[44e] Khromova et al.^[44f] have also tested the effect of the Ni content on NiCu/SiO₂ catalysts by using anisole as a model compound. In all cases, the catalysts appear to be most selective toward ring saturation. Increasing the Ni content increases coke formation, likely as a result of interactions with the aromatic rings. Copper-rich (15 wt% Ni and 85 wt% Cu-based on active-phase alone) catalysts are more selective towards hydrogenolysis reactions than nickel-rich catalysts (85 wt% Ni); however, the conversions are capped at 80% compared to 100% for the nickel-rich catalyst.^[44f] Evidently, the use/development of NiCu catalysts appears to be conflicted and further research is warranted.

Compared to the addition of Cu to active metals, the addition of Fe is also appealing and is gaining popularity. Upon successfully demonstrating the use of NiFe for furanic compounds (see Section 4.2.), Nie et al.,^[25a] later reported the use of NiFe with *m*-cresol. At 300 °C and atmospheric pressure, the addition of 5 wt% Fe to 5 wt% Ni decreases the conversion from 16.2 to 13.7%. However, the selectivity towards toluene increases from 14.2 to 52.6 wt%, whereas the selectivity towards saturated-ring products decreases to 0%. Notably, transalkylation reactions are also observed on the NiFe catalyst. The authors propose that, in comparison to the Ni catalyst, which adsorbs the phenolic compound by the ring, the addition of Fe causes the compound to adsorb vertically by the oxygen atom upon tautomerism of the hydroxy group into a carbonyl group, which promotes the DDO reaction route.^[25a] Nevertheless, they suggest that alloying active metals with oxophilic metals reduces ring interactions and increases interactions with oxygen-containing groups.

Similarly to NiFe, the combination of Fe and Pd has also undergone extensive investigations.^[25b, 44c, d] Sun et al.^[25b] have studied the deoxygenation of vapor-phase guaiacol over a PdFe/C catalyst. In their work, Pd is selected over Pt and Ru because it is less active in ring-opening reactions. A catalyst containing 2 wt% Pd and 10 wt% Fe attains a yield of oxygen-free compounds of 25.9% compared to a 10 wt% Fe catalyst that achieves a yield of 6.3% and a 5 wt% Pd catalyst that achieves a yield of 2.7%.^[25b] The overall conversion of guaiacol with the PdFe catalyst is comparable to that obtained with the 5 wt% Pd catalyst. Unlike precious-metal catalysts, the PdFe catalyst favors DDO reactions and experiences no ring-opening/ring-saturation reactions.^[25b] Through DFT calculations it was found that, compared to Pd and Fe individually, pairing of the two metals as the catalyst results in a weaker bond between the aromatic ring and the catalyst surface.^[25b] It is proposed that the function of the catalyst is such that Fe facilitates the adsorption of the oxygenated compound, whereas Pd facilitates H₂ disassociation and the reduction of the iron oxide that is developed during DDO.^[25b] This synergistic behavior between PdFe has been further studied by Hong et al.,^[44d] who demonstrate a hydrogen spillover from Pd to Fe, which can also be applied to other noble metals with results expected to follow the order of H₂ sticking probability.

Hensley et al.^[44c] propose a catalytic mechanism for the DDO on PdFe. Through DFT calculations, the most likely catalytic mechanism is dehydroxylation. In contrast to Nie et al.,^[25a] who propose adsorption occurs on the Fe atom vertically, Hensley et al.^[44c] suggest that phenolic compounds are more stably adsorbed onto the surface in a more horizontal fashion with weak bonds to the aromatic ring. With phenol as a model compound, the tilted/horizontal adsorption mechanism facilitates the direct removal of the hydroxy group to produce an adsorbed phenyl group.^[44c] Benzene and water are then produced upon subsequent hydrogenation and desorption (see Scheme 7).

Other bimetallic catalysts that have received attention include PtSn, PtNi, PtCo, PtRe, and NiCo.^[44a, b, e, 45] The addition of oxophilic Sn to Pt is expected to behave in a manner similar to the addition of Fe to activate metals. González-Borja and Resasco^[44b] report that a PtSn catalyst possesses higher initial activity than a Pt catalyst. The addition of either Ni or Co to Pt increases the overall activity of the catalysts; however, these cat-



Scheme 7. Adsorption of phenol on Pd compared to the adsorption and dehydroxylation of phenol on PdFe.^[38c]

alysts promote the production of saturated-ring products.^[44a] Ohta et al.^[45] have studied the deoxygenation of 4-propylphenol at 280 °C in an aqueous environment and report that, under such conditions, the addition of Re stabilizes Pt and provides higher conversions than the addition of other oxophilic metals such as Sn and Fe. Huynh et al.^[44e] also demonstrate that the addition of Co to Ni does not effectively promote DDO, as both the Ni and NiCo catalysts promote ring-saturation reactions. However, it is noted that the addition of Co to Ni decreases the Ni particle size, which increases the conversion and helps to prevent catalyst deactivation through coke deposition.

3.2.2. Catalyst support

Overall, there appears to be a lack of comprehensive studies that investigate the effect that the support has on the deoxygenation of phenolic compounds. As a result, additional research is required to clarify the role of catalyst supports. The most common supports that have been considered for the deoxygenation of phenolic compounds include acidic supports such as the reducible oxide supports first introduced in Section 2.2 and activated carbon. Of these supports, acidic supports such as Al₂O₃ and ZrO₂ have received a lot of attention.

A variety of authors have indicated that the combination of a noble-metal catalyst and acidic support can be very beneficial for the deoxygenation of phenolic compounds.^[1a,29,46] Contrary to the high interest in acidic supports, Al₂O₃ has recently been ruled out as a viable support.^[5] As mentioned earlier, bio-oil tends to contain a significant amount of water, and the catalytic deoxygenation of phenols produces a significant amount of water as well. In the presence of such a high amount of water, Al₂O₃ is converted into boehmite [Al₂O(OH)], which reduces the activity of the active material by oxidation.^[5b,33b]

On the other hand, ZrO₂ as a weaker acidic support has been deemed more suitable. De Souza et al.^[47] report that the use of ZrO₂ as a support for Pd behaves similarly to the addition of an oxophilic metal to an active metal, as Pd/ZrO₂ favors the production of toluene from *m*-cresol at 300 °C and atmospheric H₂ pressure.^[47] Ohta et al.^[45] compare various supports (ZrO₂, Al₂O₃, TiO₂, CeO₂, and SiO₂) for their PtRe catalyst in an aqueous environment at 280 °C and demonstrate that the ZrO₂-supported catalyst offers higher conversions (67%), whereas SiO₂ is the least-active catalyst (8.1% conversion).^[45] However, they report an environment with such a high water concentration that the catalyst deactivates dramatically owing to structural changes in ZrO₂ and subsequent wrapping of the Pt particles. No such deactivation is reported if water is not used as the solvent.

Work performed by Mortensen et al.,^[48] however, contradicts the notion that the addition of an active metal to a reducible support promotes the DDO reaction pathway. They report that at a temperature of 275 °C and H₂ pressure of 100 bar, their Ni catalysts on supports such as ZrO₂ and CeO₂ promote the HYD reaction pathway. ZrO₂ converts phenol into cyclohexanol, whereas supports containing CeO₂ mainly produce cyclohexanol. The massive differences observed in the reaction pathway

selectivity may be attributed to the highly reductive environment that is employed by Mortensen et al.^[48] relative to that used in the work performed by De Souza et al.^[47] Clearly, a higher H₂ pressure may favor the kinetics of the HYD pathway over DDO. A higher H₂ pressure may also lead to the production of more oxygen vacancies on the support, which thus increases its acidity.

Currently, on the basis of the limited literature available, it can be claimed that catalysts supported on mildly acidic materials are expected to provide the most desired results. However, carbon supports may be more stable than acidic supports.^[5a] The use of activated carbon has been demonstrated for other deoxygenation processes (to be discussed in Section 4) and has been found to promote reactions that require a minimum amount of H₂.^[1a] This warrants future studies on the impact of carbon as a support with a comparison to acidic supports such as ZrO₂.

4. Furanic Compounds

Furanic compounds such as furfural and 5-hydroxymethylfurfural (HMF) are produced from cellulose and hemicellulose through dehydration reactions, which may occur during thermal processing. These compounds are characterized as having a carbonyl group and, in the case of HMF, a hydroxymethyl group attached to a furanic ring. The conversion of these compounds into 2-methylfuran (2-MF) and 2,5-dimethylfuran (2,5-DMF) is becoming increasingly popular amongst researchers.^[1a,7] This is because these compounds have been shown to be potentially viable subjects for blending with gasoline owing to comparable properties and higher energy densities than ethanol ($\approx 40\%$ greater for 2,5-DMF).^[49] In addition, 2,5-DMF has received attention in the chemical industry as a potential precursor for *p*-xylene.^[7] Figure 3 lists various important furanic compounds.

The challenge of producing 2,5-DMF and 2-MF from HMF and furfural is in line with the topics discussed in this paper, that is, selective deoxygenation while minimizing H₂ consumption by restricting ring saturation.^[1a] Comparatively, completely saturated C₄–C₆ hydrocarbon ring-opening products are

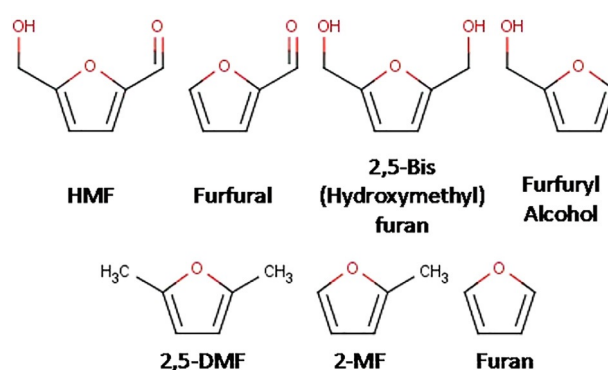
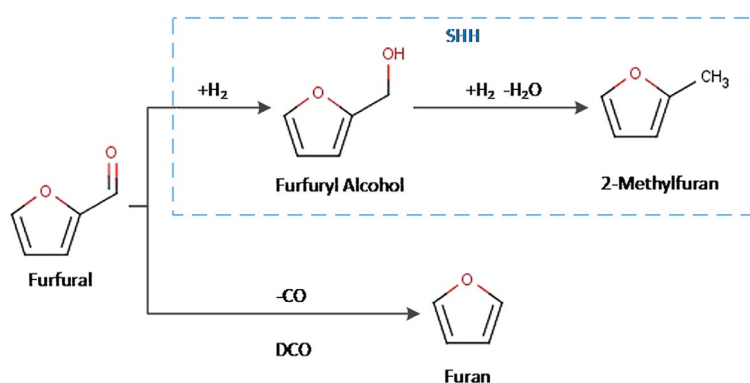


Figure 3. Structures of important furanic compounds involved in the selective deoxygenation process.

viewed as byproducts having lower value, as they are not suitable for use as transportation fuels.^[7]

4.1. Reaction mechanisms

During the selective deoxygenation of furfural and HMF, whereby the aromatic structures are retained, the three main reactions that may occur are hydrogenation of the C=O bonds, decarbonylation (DCO), and hydrogenolysis of C–O bonds. Selective hydrogenation/hydrogenolysis (SHH) reactions utilize surface hydrogen effectively to convert carbonyl groups into hydroxymethyl groups and eventually into methyl groups (see Scheme 8).^[49b,c,50] Similar to fatty acids, increasing the temperature may have an impact on the selectivity towards the DCO and SHH reaction pathways, as the former is endothermic, whereas the latter is exothermic.



Scheme 8. DCO versus SHH of furfural.

4.1.1. Deoxygenation of carbonyl groups

Decarbonylation, which stoichiometrically does not require H₂, has been found to occur if a carbonyl group-containing furanic substrate is adsorbed onto a catalyst by the furan ring, which subsequently leads to the adsorption of the carbonyl group.^[50a] Pang and Medlin^[50a] report that the hydrogen atom on the carbonyl group is first abstracted by the catalyst, which is followed by C–C scission to produce CO and a strongly adsorbed furyl ring, which must be hydrogenated before desorption.

It has been proposed that C=O hydrogenation may also occur from the same initial adsorbed intermediate.^[50c,51] Hydrogenation of the C=O group produces 2,5-bis(hydroxymethyl)furan (2,5-BHMF) from HMF or furfuryl alcohol from furfural. Regardless, the hydrogenation of the C=O bond to a C–OH bond must begin with its adsorption on the catalyst surface. However, this is most predominant if the compound is adsorbed onto the catalyst surface strongly by the carbonyl group, as strong interactions with the aromatic ring tend to lead to DCO, ring-saturation, and/or ring-opening reactions.^[49c,50c]

4.1.2. Deoxygenation of hydroxymethyl groups

Hydroxymethyl groups attached to furan rings may not undergo deoxygenation through simple dehydration reactions owing to the lack of an α -hydrogen atom. Instead, to produce methyl groups, the hydroxymethyl groups must be reduced by a hydrogenolysis reaction pathway.^[49b,50b,52] Sitthisa et al.^[50c] describe the hydrogenolysis reaction as occurring if the alcoholic compound is adsorbed at the oxygen atom of the hydroxymethyl group. For this mechanism to work, 2-MF or 2,5-DMF would be produced after saturation of an adsorbed intermediate that is bound with the furanic oxygen atom.^[53] Consequently, it may be possible that upon starting from a carbonyl group, the intermediate hydroxymethyl group may remain adsorbed and directly undergo subsequent hydrogenolysis. Jenness and Vlachos^[53] propose another possible mechanism, in which the furan ring is first activated through partial hydrogenation on the α -hydrogen atom, which essentially enables a dehydration reaction to occur; however, they do not successfully demonstrate this on a Lewis acid site of a RuO_x species because of the formation of the conjugate base. Owing to limited literature, the catalytic mechanism for the hydrogenolysis of hydroxymethyl groups on furan rings requires additional clarification.

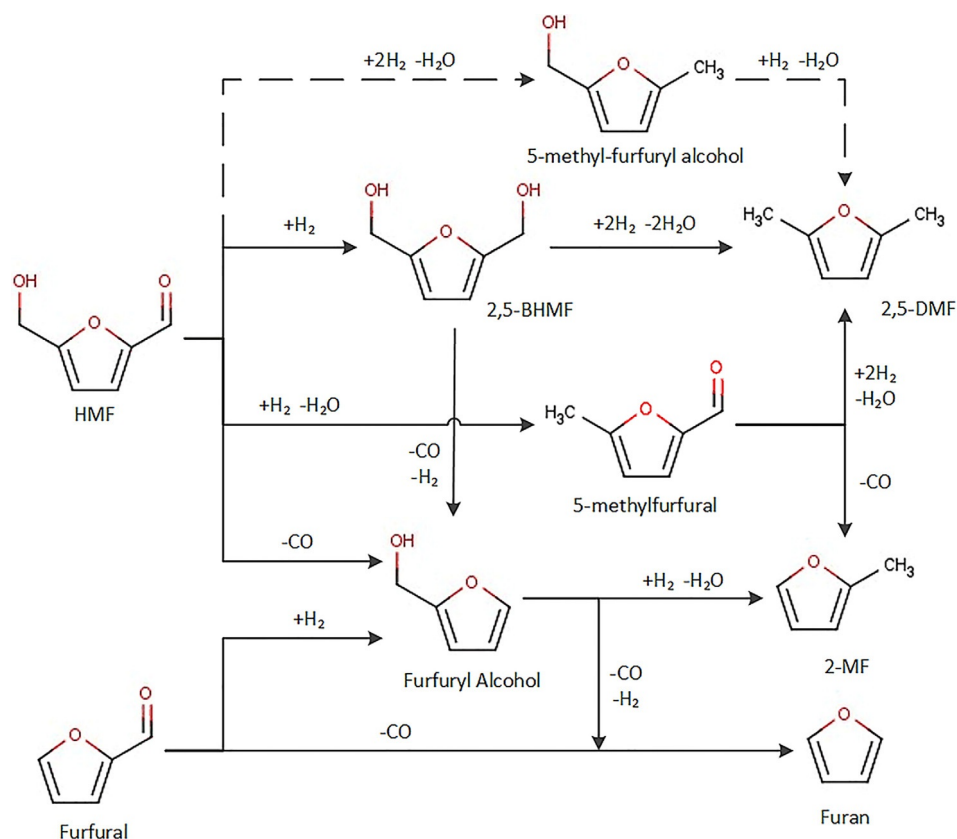
Alternatively, existing hydroxymethyl groups may undergo DCO. Pang and Medlin^[50a] also propose that upon dehydrogenation, an adsorbed hydroxymethyl group may be converted into an adsorbed carbonyl group and undergo DCO while producing H₂. This is also described by Zheng et al.^[50e] and Sitthisa et al.,^[50c] who attribute this effect to a strong interaction between the catalyst and the furan ring.

4.1.3. Summary of reaction pathways

Scheme 9 summarizes all of the reaction routes of HMF and furfural that have been discussed for the deoxygenation of carbonyl and hydroxymethyl groups. As suggested earlier, there are two overall routes for furfural: SHH, which leads to 2-MF, and DCO, which leads to furan. HMF, on the other hand, has three overall reaction routes: SHH of both functional group produces 2,5-DMF, DCO of both functional groups produces furan, and a combination of the SHH of the hydroxymethyl group and DCO of the carbonyl group produces 2-MF.

4.2. Catalyst selection

Conventional sulfide catalysts have received far less attention for the deoxygenation of furanic compounds than for the deoxygenation of fatty acid and phenolic compounds. This is likely due to the fact that a sulfur-containing compound (such as H₂S) must be co-fed to the system in order to maintain catalyst activity. Instead, much work has been done to develop new catalysts that are selective to reducing substituted hydroxymethyl and carbonyl groups without performing ring-opening reactions. Studies in the development of catalysts for



Scheme 9. Overall selective deoxygenation of HMF and furfural.

the reduction of HMF, furfural, or subsequent products such as furfuryl alcohol have been performed at temperatures ranging from 180 to 260 °C and even as high as 350 °C and typical H₂ pressures of 10–40 bar.^[1a,7] Typical catalysts that have been studied include monometallic catalysts and a variety of bimetallic catalysts.

4.2.1. Active material

4.2.1.1. Monometallic catalysts

Monometallic Ni catalysts have been ruled out for the possible selective deoxygenation of furfural and HMF while retaining the furan ring, as Ni reportedly interacts too strongly with the furan ring and promotes decarbonylation and hydrogenolysis, which lead to the opening of the ring structure.^[49c,50c,54] Given that Ni is very predominant at activating hydrogen on its surface, Ni is also known to promote saturation of the C=C bonds in the furan ring, which thus decreases the selectivity and increases H₂ consumption.^[54] Overall, at lower temperatures (210 °C), Ni catalysts favor hydrogenation reactions of the furan ring or even just the reduction of the oxygenated substituent to a methyl group (at low conversions, however). At higher temperatures (250 °C), Ni becomes selective towards DCO and ring opening.^[49c]

Similar to Ni, noble metals such as Pt and Pd have also been shown to interact with the furan ring.^[49c,50a,55] Consequently,

these catalysts favor DCO reaction routes.^[50a] This is described in detail by Pang and Medlin for a Pd catalyst;^[50a] they report that both hydroxymethyl and carbonyl groups are reduced by DCO as a result of strong interactions with the furan ring. It is suggested that ring-opening reactions may also occur as a result of such interactions. Wang et al.^[56] support the notion that a Pd catalyst can promote ring-opening reactions, as they describe ring opening to occur as a result of ring activation owing to partial hydrogenation.

Unlike Ni and noble metals, HMF and furfural adsorb onto Cu through the carbonyl group only; there is no interaction with the furan ring.^[49c] This successfully leads to the hydrogenation of the C=O bond to C–OH and potentially hydrogenolysis to a methyl group. Sitthisa and Resasco^[49c] report a Cu catalyst that is able to achieve moderate conversion (≈ 50 –75%) of furfural within a temperature range of 230 to 290 °C (depending on the ratio of feed to catalyst). However, they report that the Cu catalyst is mostly selective towards initial hydrogenation to furfuryl alcohol (yields as high as 71%) rather than 2-MF (yields as high as 8.2%).^[49c] Incorporating Ru or CrO₄ with Cu, however, is selective towards the production of 2,5-DMF from HMF with a selectivity of 79 or 61%.^[49b]

4.2.1.2. Bimetallic catalysts

The development of bimetallic catalysts, such as PtSn and NiFe (as discussed in Section 3.2.), is becoming a very popular with

researchers in the development of selective deoxygenation catalysts for deoxygenating furanic compounds. Similar to the use of bimetallic catalysts for phenolic compounds, most bimetallic catalysts are appealing because of their selective ability to deoxygenate oxygen-containing functional groups attached to an aromatic ring whilst hindering major interactions with the aromatic ring. On top of that, various studies suggest that the addition of an oxophilic metal with an active metal can help to improve selective deoxygenation.^[49c,50c,d] Oxophilic metals promote the adsorption of carbonyl groups, which minimizes catalyst–ring interactions. The hydrogen that is transferred from the active metal effectively reduces the C=O bond, which possibly produces a methyl group.

The combination of Fe and Ni to form a bimetallic NiFe catalyst, which was first described in Section 3.2., has received much attention for the selective deoxygenation of furfural and HMF. It has been widely demonstrated that the addition of Fe successfully reduces interactions between Ni and the furan ring while promoting SHH reactions.^[50c,d,57] Sitthisa et al.^[50c] report that at 250 °C and 1 bar (H_2 /feed ratio = 25), the addition of 2 wt% Fe to 5 wt% Ni on SiO_2 increases the yield of 2-MF produced from furfural from < 10% to as high as 39.1%.^[50c] Yu et al.^[57a] have tested NiFe for the selective deoxygenation of HMF with various ratios of Ni/Fe. All NiFe and Ni catalysts show conversions as high as 100%. The highest selectivity (91.3%) towards DMF is achieved with a Ni/Fe ratio of 2 at a temperature of 200 °C. No ring opening is observed over the NiFe catalyst. Comparatively, Ni catalysts are only able to achieve a DMF selectivity as high as 8.1% with the balance attributed to oxygenated furanic compounds and saturated-ring products.^[57a] The NiFe (2:1 ratio) catalyst is also noted as being relatively stable and can be reactivated by a calcination process. Deactivation is suggested to occur as a result of the slow formation of polymeric humins, which cover the catalyst surface.^[57a]

Yu et al.^[57b] propose that furfuryl alcohol is produced as an intermediate of furfural if using NiFe. They demonstrate that upon adding Fe, there is a strong interaction between the C=O bond and the catalyst surface; however, there are also interactions with the furan ring. It is reported that on Ni, the furan ring of furfural is adsorbed more parallel to the Ni(111) surface, whereas on the FeNi(111) surface, the furan ring is more tilted (see Figure 4).^[57b] This, in combination with the strong interaction with the oxygen-containing constituents on the furan ring, favors conversion into 2-MF. In a later study, Yu and Chen^[50d] also suggest that the aromatic ring of furfural may still adsorb onto the catalyst surface along with the carbonyl

group, which can result in some DCO reactions. This would likely be dependent on the Fe content.

Other bimetallic catalysts that have been investigated include the addition of various metals (e.g., Co, Re, Sn, and Zn) with Pt, NiPd, PdCu, and Rh/Ir catalysts modified with RuO_x . Chen et al.^[58] have studied the use of NiPd, PtRe, PtSn, and PtIn catalysts for the selective reduction of furfural to furfuryl alcohol. NiPd favors ring saturation, which produces tetrahydrofurfuryl alcohol in yields as high as 93.4%. PtRe (2 wt% Pt and 1 wt% Re) is the most selective towards the reduction of furfural to furfuryl alcohol with a selectivity of 95.7% at a conversion of 100%. Comparatively, PtSn achieves a furfuryl alcohol selectivity of 47.8% at 98.3% conversion, whereas PtIn achieves a selectivity of 74.9% at a conversion of 73.3%.^[58] On the basis of these results; with further optimizations, PtRe may be a viable catalyst for the production of 2-MF from furfural.

Much like the addition of Re to Pt, Lesiak et al.^[59] demonstrate that the addition of Cu to Pd also hinders ring-saturation reactions.^[59] Eventually, PtSn may also become a competitive option, as this catalyst has received conflicting results. For example, Merlo et al.^[60] use PtSn to produce furfuryl alcohol from furfural at high selectivities (96–98%).

Surprisingly, another catalyst to consider is the addition of Co to Pt.^[56,61] Although Co is not known as an oxophilic metal, Wang et al.^[56] report a 100% conversion of HMF with a DMF yield of 98% with their PtCo catalyst. The reason for the decrease in catalyst–ring interactions relative to that observed for Pt catalysts is currently not well understood.

Although there has yet to be any significant experimental work done with the use of PtZn as a catalyst for the reduction of furanic compounds, it is likely that such a catalyst will receive much attention in future work. Shi and Vohs^[62] present insight into the reaction mechanism by which furfural would be reduced on a PtZn catalyst. They calculate that, similar to other combinations of active and oxophilic metals, furfural primarily bonds through the carbonyl group of furfural. In contrast, they propose that rather than producing furfuryl alcohol as an intermediate, as suggested by Yu et al.^[57b] for a NiFe catalyst, furfural undergoes a direct oxygen-removal reaction.^[62] The resulting product is adsorbed onto the catalyst through a di-unsaturated methyl group attached to the furan ring. Subsequent hydrogenation and desorption produces 2-MF and water.

The mechanism described by Shi and Vohs^[62] closely resembles the catalytic mechanism for phenol on a bimetallic catalyst containing an active metal phase and an oxophilic metal, as described by Hensley et al.^[44c] On monometallic catalysts, both furanic and phenolic catalysts reportedly favor adsorption and interaction with the aromatic rings, which leads to saturation and possibly ring opening. For both types of compounds, adding a second oxophilic metal changes the adsorption behavior to favor the adsorption of the compounds primarily through the oxygen-containing constituents; this causes the aromatic rings to tilt away from the surface. Unlike furfural, 5-HMF has both a carbonyl group and hydroxymethyl group, which may present a competitive adsorption mechanism. This competitive nature is yet to be studied thoroughly. It is be-

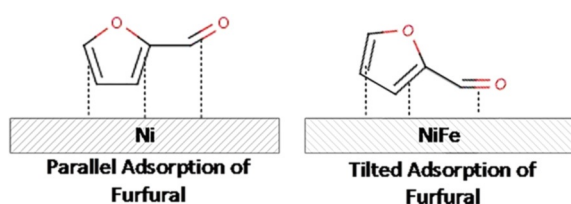
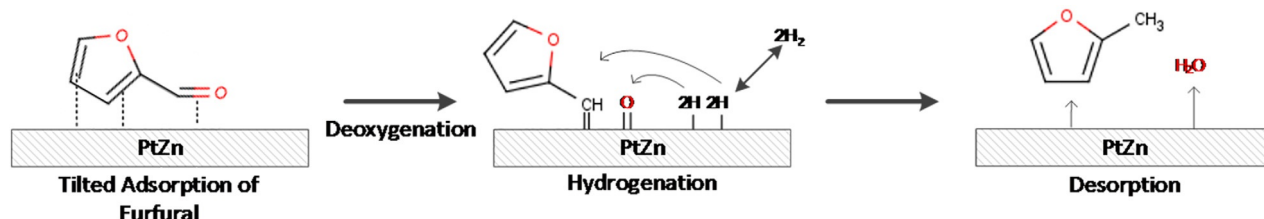


Figure 4. Adsorption of furfural on NiFe compared to Ni.^[57b]



Scheme 10. Deoxygenation of furfural on PtZn.^[63]

lieved that 5-HMF favors adsorption through the carbonyl group, which upon subsequent direct deoxygenation (similar to that described in Scheme 10) produces 5-methylfurfuryl alcohol (see Scheme 9).

The development of bimetallic catalysts with a metal-oxide catalyst such as RuO_x is currently conflicted. Tamura et al.^[63] have developed an Ir–RuO_x catalyst that is active towards hydrogenolysis and selective towards hydrogenation owing to the formation of a hydride species. However, Rh–RuO_x and Ir–RuO_x catalysts also promote ring-opening reactions of tetrahydrofurfuryl alcohol owing to a hydrogen-transfer reaction from the hydroxymethyl group.^[64]

In a H₂-free environment, deoxygenation of HMF or furfural appears possible over catalysts such as Ni and noble metals owing to their strong interactions with the furan ring. This would produce furan, CO, and, in the case of HMF, H₂. However, furan may not be as desirable as 2-MF and 2,5-DMF, and in addition, ring-opening reactions and catalyst deactivation are also likely scenarios. Although selective deoxygenation reduces H₂ consumption, 1 mol of HMF still requires 3 mol of H₂ to be converted into 2,5-DMF. Therefore, to minimize H₂ consumption, it may be most favorable to proceed with a balance between DCO and selective hydrogenolysis reactions to produce 2,5-DMF, 2-MF, and furan from HMF (to be discussed more in Section 5). A NiFe bimetallic catalyst may be a potential candidate for such an application, as it promotes selective hydrogenation and hydrogenolysis and has some activity towards DCO reactions.

4.2.2. Catalyst support

The effect of using various different catalyst supports for the selective deoxygenation of furanic compounds has received very little attention. Most research studies focus on catalysts based on neutral SiO₂ or carbon supports. For the most part, acidic catalyst supports should be avoided, especially if not saturating the furan ring. This is because acidic catalysts promote rearrangement and polymerization reactions, which can quickly lead to catalyst deactivation.^[7] Polymerization of HMF, furfural, and their derivatives reportedly occurs on acidic catalysts if hydrogenation is slow or does not occur.^[7,65] Thus, limiting the contact time and, inadvertently, reducing conversion, is required in such a case.

Catalyst supports such as TiO₂ and Fe₂O₃, however, have been receiving some attention owing to their interactions with active metals.^[7,50b,66] As elucidated in Section 3.2., catalysts that demonstrate strong metal–support interactions promote selec-

tive hydrogenation/hydrogenolysis reactions in a fashion similar to that of oxophilic metals added onto active metal catalysts.^[66] Scholz et al.^[50b] report that Pd and Ni supported on oxophilic Fe₂O₃ alters the reaction pathway of the Pd catalyst from favoring strong interactions with the furan ring to favoring SHH reactions of the carbonyl and hydroxymethyl groups on HMF. However, they also witnessed saturated-ring products, which may be due to extended catalyst contact times. Notably, these reactions involve catalytic hydrogen transfer rather than hydrogenation. Owing to the decent performance of NiFe bimetallic catalysts observed in the previous section, it would be interesting to see how well a Ni/Fe₂O₃ catalyst would perform for the selective deoxygenation of furfural/HMF with a limited amount of atmospheric H₂. Active metals supported on ZrO₂ may also be a viable option, as they have been shown to be successful for similar use with phenolic compounds. However, care would have to be taken with regard to acidity.

5. Discussion—Future Work and New Implications

5.1. H₂-free versus H₂-modest environments

It has been shown that there is a plethora of work being done to minimize the consumption of H₂ in the catalytic deoxygenation of vegetable oils, phenolic compounds, and furanic compounds. The general consensus is that, depending on the compounds, it is theoretically possible to perform deoxygenation without the presence of H₂. However, H₂ is typically involved in the reactions in some way, and thus, without H₂, low conversions, high catalyst deactivation, and undesired products are expected.

The deoxygenation of vegetable oils has a problem at the very first step—the β -elimination reactions require H₂ for complete conversion. One alternative could possibly be to promote hydrolysis reactions for the breakdown of triglycerides. Owing to a lack of research done for the use of hydrolysis, it is not clear how viable such an alternative would be. One would have to consider the impact of glycerol as a byproduct, as it is unusable as a direct fuel, and how elevated concentrations of water would affect subsequent deoxygenation reactions. To address these issues, it may be appropriate to conceive a two-step process, in which triglycerides are broken down into fatty acids in one reaction step followed by fatty acid deoxygenation in a second reaction step. Such a process would likely require separation stages between the two reaction steps. Such a two-step process would closely resemble a process used to

produce FAME biodiesel, such as the process described by Kusdianna and Saka.^[67] Notably, some researchers have begun to develop hydrothermal processes for the deoxygenation of fatty acids in addition to the possibility of a one-step hydrolysis–deoxygenation process.^[6,12,68]

In any case, the deoxygenation of fatty acids presents a challenge of its own. Although the deoxygenation of fatty acids without H₂ is possible through DCO_x, deactivation is an issue. H₂ is, therefore, required to fully break down triglycerides into vegetable oils and to maintain activity. In addition, indirect DCO reactions appear to be much faster than direct DCO reactions. Having some H₂ available would promote indirect DCO, which would likely improve the conversion.

Similarly, the deoxygenation of furanic compounds can be done without H₂; however, H₂ is still required to maintain catalytic activity. In addition, the furan produced through the deoxygenation of HMF or furfural without H₂ may not be as desirable as products such as 2,5-DMF and 2-MF that can be produced by selective deoxygenation in the presence of a minimal amount of H₂. Undesired ring-opening products are also a possibility.

Phenolic compounds, on the other hand, definitely need a source of hydrogen atoms to remove oxygen. Given that there is no reaction pathway that removes oxygen as CO or CO₂, hydrogen is required to remove oxygen selectively as water. In addition, an onslaught of catalyst deactivation is brought upon the catalyst's inability to hydrogenate oxygen and carbon structures that are strongly adsorbed on the catalyst surface. Oxygen that is not hydrogenated to water effectively oxidizes the catalyst, whereas the carbon pools that are not saturated lead to coking.

To achieve desirable products by catalytic deoxygenation, a limited amount of H₂ should be available. Thus, H₂-modest systems should be applied rather than H₂-free systems. The amount of H₂ that is used should be less than conventional, nonselective deoxygenation processes, ideally at near-stoichiometric amounts or enough to maintain catalyst activity.

5.2. Insight into future catalyst developments

Throughout this review, various catalysts have been identified as being appropriate (or inappropriate) for H₂-modest processes. However, it has been observed that the catalysts that have been studied tend to differ between researchers depending on which resource they are focusing. For example, researchers in the field of vegetable oils focus on the use of metal-sulfide, noble-metal, and common transition-metal catalysts such as nickel. On the other hand, phenolic compounds have seen the development of metal-oxide and transition-metal phosphide catalysts, whereas both furanic and phenolic compounds have seen significant developments with bimetallic catalysts. Overall, it appears as though all three resources benefit from the use of catalysts containing bifunctionality—the ability to adsorb the compounds through the oxygen-containing functional groups and the ability to activate H₂.

In Section 2, it was discussed that to minimize H₂ consumption, one should consider the promotion of DCO_x reaction

pathways. Of all DCO_x reaction pathways, indirect DCO, which requires the presence of H₂, appears to be the fastest reaction. Direct DCO or DCO₂ reactions are hindered in the presence of H₂, and they present a mechanism by which catalyst deactivation may occur quickly. To perform indirect DCO, the first step is a hydrogenolysis reaction into an aldehyde intermediate, which is followed by DCO. One catalyst that appears to benefit this reaction route is Ni/ZrO₂. This is because of a synergistic effect and/or the bifunctionality of the catalyst that supports the hydrogenolysis step.

The use of an active metal such as Ni on a reducible support such as ZrO₂ was also discussed in Sections 3.2 and 4.2. In these sections, it was elucidated that the catalysts are very comparable in function to bimetallic catalysts containing an active metal and an oxophilic metal such as NiFe. It is, therefore, suggested that future work be done to explore the use of such bimetallic catalysts for the deoxygenation of fatty acids. It is predicted that a catalyst such as NiFe or PdFe will promote the adsorption of fatty acids through the oxygen atoms, which will lead to direct removal of said oxygen. To enable the subsequent DCO reaction, the catalyst will likely need to maintain some monometallic properties. It is, therefore, suggested that for applications involving with fatty acids, these catalysts should have a lower oxophilic-to-active metal ratio (Fe–Pd ratio, for example) compared to similar catalysts used with phenolic and furanic compounds.

Another type of catalyst that may present the necessary bifunctionality properties for the deoxygenation of fatty acids would be a transition-metal phosphide catalyst. It is expected that a phosphide catalyst such as Ni₂P would also be comparable to a catalyst such as Ni/ZrO₂. As Cecilia et al. concluded in 2013, Ni₂P functions in a manner similar to that of active metals on acidic supports and exhibits both metallic and acidic properties, which would be necessary for indirect DCO.^[36] Indeed, some work has already been performed, and it has been demonstrated that Ni₂P promotes DCO_x reactions.^[69] Additional research would be beneficial to understand how such a catalyst compares to other catalysts that have been studied for the deoxygenation of vegetable oils.

In Sections 3 and 4, several comparisons were made with regard to the development of catalyst for the deoxygenation of furanic and phenolic compounds, especially for bimetallic catalysts. To minimize H₂ consumption, both types of compounds appear to require the same treatment, that is, selective deoxygenation of oxygen-containing constituents while minimizing ring-saturation and ring-opening reactions. Bimetallic catalysts such as NiFe and PdFe appear to be suitable selections for achieving these goals. In addition, there are not enough investigations towards the use of different catalyst supports. Therefore, it is recommended that future studies explore the use of active metals supported on reducible oxides. The use of various combinations of reducible oxides such as CeO₂ and ZrO₂ is also very interesting. A support with enhanced oxygen-storage capacity, as reported for CeO₂ and ZrO₂, with a highly dispersed active metal phase would likely be beneficial for the selective deoxygenation of furanic and phenolic compounds. As stated in Section 4.2., care should be

taken with regard to catalyst acidity upon deoxygenating furanic compounds, as it may lead to rapid catalyst deactivation owing to polymerization reactions.

In the development of catalysts for phenolic or furanic model compounds, it is important that researchers consider whether or not the catalyst would also be appropriate for both model compounds. This is because phenolic and furanic compounds, as well as various other compounds, exist together in bio-oil and are treated together rather than separately. Thus, a catalyst that is selected for deoxygenating HMF should also be stable for the deoxygenation of guaiacol.

5.3. Additional strategies for reducing fossil-fuel-derived H₂ dependence

Throughout this review, the major strategy for reducing the requirement of H₂ has been to perform selective deoxygenation to reduce H₂ consumption. Other strategies that are currently undergoing research include the production of H₂ from renewable sources and the use of internal hydrogen, otherwise known as in situ hydrogen.

5.3.1. External sources of hydrogen

The production of H₂ through processes such as gasification of biomass has received some attention as a potential candidate for a supply of H₂ for deoxygenation processes. However, there are concerns regarding the costs associated with the actual process of gasifying the biomass then purifying the H₂ for use in a hydrotreater. As an alternative, Tanneru and Steele^[70] propose the use of syngas directly for the purpose of deoxygenation. The use of syngas is successful for performing the initial steps of the catalytic deoxygenation of bio-oil with results that are comparable to those obtained with the use of pure H₂. The success of this process is partly attributed to the water–gas-shift reaction, which will be discussed in greater detail below.^[70] With further optimizations in terms of the catalysts and conditions, it is possible that the direct use of syngas may become a viable option for industrial application.

5.3.2. Internal sources of hydrogen

Internally sourced hydrogen, or in situ hydrogen, is H₂ (or hydrogen atoms in general) that is produced and used for reaction in the same reactor. There is no external supply of H₂ gas. An example of a system that uses in situ hydrogen is the use of a hydrogen-donor solvent to produce hydrogen atoms on the catalyst surface. Another example that is presented here for the first time as a potential source of in situ hydrogen and a major contributor to reducing H₂ consumption is the promotion of the water–gas-shift and steam-reforming reactions.

5.3.2.1. Hydrogen-donor solvents

The use of proton-donor solvents such as biomass-derived acids and alcohols is becoming popular, as they reduce the reliance on H₂ from fossil fuels and are, for the most part, easier

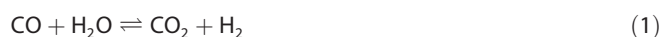
and safer to store at isolated locations than H₂.^[50b] The most common donors that have been considered are formic acid and light alcohols such as propan-2-ol.^[50b,71] The basic idea behind proton-donor solvents is that hydrogen atoms are abstracted from the organic molecule and activated on the catalyst surface. For formic acid, this occurs through decomposition into H₂ and CO₂.

Alcohols donate hydrogen through the disassociation of a hydrogen atom from the hydroxy group, which produces its conjugate ketone, such as acetone for propan-2-ol. The results for the use of propan-2-ol with furfural from Scholz et al.^[50b] are moderate. In some cases, high conversions of furfural and HMF are observed; however, the reactions are mostly selective towards the production of hydroxymethyl groups.^[50b] With future reaction and catalyst optimizations, it may be possible to increase the selectivity towards the production of methyl groups. On the other hand, Reddy et al.^[71e] report decent conversions of furfural and *p*-cresol over Ni–Cu catalysts by using propan-2-ol as a hydrogen donor. Deoxygenation is not significant, however, in tests performed with real bio-oil. In this case, propan-2-ol undergoes esterification with short acids such as acetic acid, which the authors conclude would help stabilize the bio-oil for further processing.

There are some concerns that need to be addressed with regard to catalytic hydrogen-transfer processes. The major concern is cost. If formic acid is selected, there is the cost associated with the procurement of formic acid, and owing to the corrosiveness of formic acid, there will also be additional capital and maintenance costs associated with its use. For alcohols, there is concern about solvent consumption and recovery. Recovering the solvent will require a subsequent separation process to retrieve the ketone followed by a reaction process to convert the ketone back into an alcohol. If, on the other hand, the alcohol is not recovered, there will be additional procurement costs. Another concern is the origin of the solvents. Given that one of the objectives of using hydrogen-donor solvents is to eliminate the reliance on the fossil-fuel industry for producing H₂, one should ensure that the solvents that are used are derived from biomass. The aforementioned concerns aside, these processes can be deemed much safer than typical hydrotreating processes, because they do not involve the storage and handling of high-pressure H₂.

5.3.2.2. Water–gas-shift and reforming reactions

One topic that appears to have been overlooked in the minimization of H₂ consumption is the consideration of water–gas-shift (WGS) [Eq. (1)] and methane steam-reforming (MSR) [Eq. (2)] reactions.

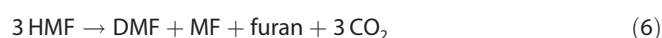


More focus needs to be made on promoting WGS under the reaction conditions to regenerate H₂ gas. Removing oxygen as both CO and H₂O is lost potential, as they can be used to produce H₂, which can be used again to remove oxygen. In Sec-

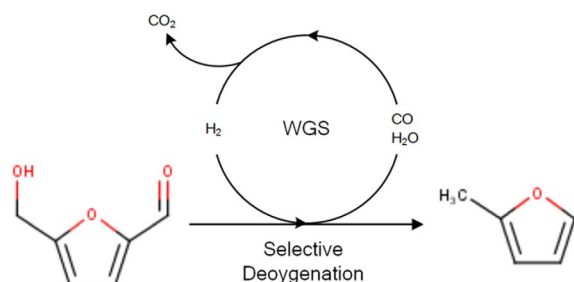
tion 4.2., it was suggested that there should be a balance between removing oxygen selectively as H₂O and CO. Looking at Equations (3)–(5), which represent the overall SHH and DCO reaction pathways presented in Scheme 8, it can be theoretically derived that equimolar amounts of CO and H₂O can be produced if 3 mol of HMF are split equally amongst the three reactions.



Assuming 100% conversions, balancing these reactions with the WGS reaction [Eq. (1)] results in no net consumption of H₂ [see Eq. (6)]. Simply, all H₂ that would be consumed would be regenerated.



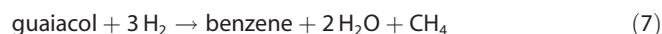
Alternatively, one could also theoretically optimize just Equations (1) and (4) to produce just 2-Methylfuran from HMF while effectively consuming no H₂ (see Scheme 11).



Scheme 11. Selective deoxygenation of 5-HMF with WGS.

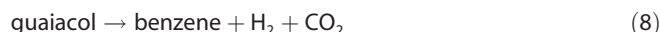
Theoretically, a very similar optimization could be conceived for fatty acids. Starting from a C_n fatty acid and proceeding through the indirect DCO reaction route to the production of a C_{n-1} paraffin, 1 mol of H₂ is consumed and 1 mol of H₂O and 1 mol of CO are produced. Balancing this with the WGS results in no net consumption of H₂ and the release of CO₂, which resembles the DCO₂ reaction.

As for phenolic compounds, as oxygen cannot be removed as CO from phenolic compounds, the WGS reaction is not directly available to regenerate H₂. Instead, the deoxygenation of phenolic compounds that have a methoxy group, such as guaiacol, can produce benzene, methane, and water [see Eq. (7)].



The presence of both methane and water would enable MSR reactions, which, as seen in Equation (2), would produce 3 mol of H₂. Therefore, assuming 100% conversion, one could theorize the production of benzene, CO, and water from guaia-

col with no net consumption of H₂. Beyond that, as CO is formed, further balancing these reactions with the WGS would actually lead to a net production of 1 mol of H₂ along with benzene and CO₂, such as that shown in Equation (8).



Notably, these reactions of guaiacol are only supported by the reaction routes that produce benzene, which is, as mentioned in Section 3, not particularly ideal. Alternatively, one could aim for the production of toluene from guaiacol, which would prevent the possibility of regenerating H₂.

Above all, the balances and ideas that have been presented here demonstrate the importance of the WGS reaction and, possibly, the MSR reaction. Although these propositions are far-fetched (such as assuming 100% conversion of even WGS and MSR reactions), they do demonstrate that more can be done to reduce H₂ consumption by producing in situ H₂. It is, therefore, proposed that future works not only look at developing catalysts and additives that promote selective deoxygenation reactions in H₂-modest environments but also look at catalysts/additives that promote WGS and MSR (or possibly other steam-reforming reactions such as propane from vegetable oils) reactions. Bifunctional catalysts that promote both deoxygenation and WGS/MSR may be ideal for such a proposal.

An appropriate initial step towards developing bifunctional catalysts would be to look at deoxygenation catalysts that contain materials known to promote WGS and MSR reactions (and vice versa) and to monitor their performances under desired reaction conditions. Ratnasamy and Wagner^[72] extensively review catalysts that are used for WGS. In industry, catalysts that are currently being used include iron oxides that are stabilized by chromium oxide (Fe₂O₃-Cr₂O₃) for high-temperature WGS (350–450 °C) and Cu-ZnO-Al₂O₃ catalysts for low-temperature WGS (190–250 °C).^[72] The addition of a promoter metal such as Ni, Pt, Pd, and Rh to iron-oxide based catalysts has been shown to improve the reaction kinetics of high-temperature WGS.^[73] Ni and Pd supported on Fe₂O₃ has been shown to promote the deoxygenation of SHH and DCO of furfural by Scholz et al.^[50b] at 180 °C with propan-2-ol as a H-donor. Therefore, promoted iron-oxide catalysts may be a potential candidates; however, one must consider the temperature difference (180 vs. 350 °C).

Although thermodynamic equilibrium is generally not a concern for the deoxygenation of HMF, it is, however, a concern for WGS, which is an exothermic reaction ($\Delta H = -41.1 \text{ kJ mol}^{-1}$). In industry, WGS first occurs through a high-temperature step ($K_p = 20.5$ at 350 °C) followed by a low-temperature step ($K_p > 100$) to help shift the equilibrium to complete conversion of CO.^[72] Although the H₂ consumption by deoxygenation may shift the equilibrium even more towards the products, operating at temperatures as high as 350 °C may not be suitable for phenolic and furanic compounds owing to the elevated possibility of coking. Therefore, the use of a low-temperature WGS catalyst may be more suitable. Unfortunately, Cu-ZnO-Al₂O₃ has not received any attention for deoxygenation.

One may also look towards catalysts used for the aqueous-phase reforming (APR) of glycerol for the production of in situ H_2 . APR of glycerol, which is derived from triglycerides, has been shown to produce H_2 , which is then used for the deoxygenation of fatty acids.^[74] In general, this is an important process to consider for the deoxygenation of vegetable oils within a hydrothermal environment, for which glycerol need not be introduced to the system, as it is produced by hydrolysis. A particular catalyst that has been shown to provide high conversions is Pt–Re/C.^[74b,c] As WGS is an important reaction within an APR process, the fact that Pt–Re/C is established as being able to perform WGS and deoxygenation makes it a potential candidate for other processes involving WGS. Using glycerol APR to produce in situ H_2 for the deoxygenation of phenolic or furanic compounds may not be suitable, because glycerol would need to be supplied from an external source. However, the APR of bio-oil that contains furanics, phenolics, and smaller compounds such as glycoaldehyde, which may undergo APR, may be another possible route of exploration.

The movement towards promoting both WGS and deoxygenation within the same catalytic process will inadvertently develop processes that are not only H_2 modest but also, to some extent, H_2 self-sufficient. The end result is a highly sustainable catalytic process that will produce desired fuels with a minimal dependence on the fossil-fuel industry.

6. Conclusions

The increasing demand for the production of biofuels through deoxygenation processes has been met with the challenge of decreasing the consumption of H_2 . There is a plethora of research work being poured into the development of catalysts that promote the selective deoxygenation reactions of vegetable oils, phenolic, and furanic compounds while consuming less H_2 . Various information gaps have been determined. Work must still be done to develop clear understandings of catalytic reaction mechanisms. An understanding of the reaction mechanisms will allow researchers to develop more selective catalysts.

On the basis of what is currently understood about reaction pathways and catalyst deactivation, it is concluded that H_2 -modest systems are more desirable than H_2 -free systems. H_2 is required because of its role in reactions and to maintain catalyst activity. The successful conversion of biomass-derived bio-oils into desired products simply cannot proceed without the presence of H_2 . That said, H_2 requirements can still be reduced by promoting reactions that lead to desired products through reaction pathways that require less H_2 .

On the basis of current knowledge, the catalysts that look promising for selective deoxygenation are those that exhibit a combination of oxophilicity and the ability to activate H_2 . Such has been found to reduce interactions between the catalyst surface and the carbon structure of oxygenated compounds while promoting the interaction with oxygen, which thereby allows for selective deoxygenation. Examples that have been explored include active metal supports for reducible

oxides such as Ni/ZrO₂ and supported bimetallic catalysts that combine active metals with oxophilic metals such as NiFe.

It has been proposed that researchers should continue to collaborate more in the development of catalysts for phenolic and furanic compounds. As phenolic and furanic compounds are to be processed together in bio-oil, it is essential that a catalyst that is proven to be viable for phenolic compounds be stable and active for furanic compounds, and vice versa.

To minimize the requirement of external sources of H_2 further, it is proposed that catalysts should not be developed on the sole basis of their ability to promote selective deoxygenation. They must be developed also to promote the production of in situ H_2 through water–gas-shift and steam-reforming reactions. The presence of CO, H_2O , and CH_4 in the outlet gas represents a missed opportunity for regenerating H_2 . Ideally, oxygen should leave a reactor as CO₂.

For vegetable oils/fatty acids, the reaction pathway that has been suggested as ideal for use in a H_2 -modest/ H_2 self-sufficient environment is the indirect decarbonylation reaction pathway. For furanic and phenolic compounds, the desired reaction routes should be based on desired products. For example, toluene rather than benzene may be the more desired product from guaiacol, as benzene is not desired for use as a fuel. However, it is noted that the production of toluene limits the possibility of regenerating H_2 , and thus, the consumption of H_2 is expected to be higher than that for the production of benzene.

Above all, researchers should focus on the development of catalysts that require the use of less H_2 and, if possible, that promote the regeneration of H_2 through the water–gas-shift and steam-reforming reactions.

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